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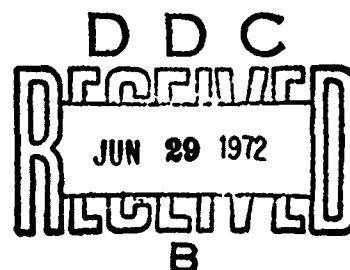
**EATR 4622**

**SPECTROSCOPIC ANALYSIS OF  
THE PRODUCTS FROM THE REACTION OF  
o-CHLOROBENZYLIDENEMALONONITRILE (CS)  
AND 2-DIETHYLAMINOETHYL MERCAPTAN (DEAEM)**

by

**Irwin Master  
Ronald J. Piffath  
Samuel Sass**

**June 1972**



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13. ABSTRACT Ultraviolet, infrared, and Raman spectra have been determined for the products of the reaction of o-chlorobenzylidenemalononitrile (CS) and 2-diethylaminoethyl mercaptan (DEAEM). Structures for two of the products, CS(DEAEM) <sub>2</sub> and (CS) <sub>2</sub> DEAEM, are given, and their spectral characteristics are discussed. Reactions were followed in the ultraviolet by observing the changes occurring in the spectrum with time. Possible reaction mechanisms are discussed for the formation of the product CS(DEAEM) <sub>2</sub> . The order of addition to CS in the case of the product CS(DEAEM) <sub>2</sub> , as observed by ultraviolet, is first, the addition to the double bond, and second, addition to the nitrile.																				
14. KEYWORDS <table><tbody><tr><td>O-Chlorobenzylidenemalononitrile</td><td>Infrared spectra</td></tr><tr><td>CS</td><td>Raman spectra</td></tr><tr><td>2-Diethylaminoethyl mercaptan</td><td>Benzylidenemalononitriles</td></tr><tr><td>DEAEM</td><td>NaCN</td></tr><tr><td>Reaction products</td><td>NaHSO<sub>3</sub></td></tr><tr><td>CS(DEAEM)<sub>2</sub></td><td>Pentanethiol</td></tr><tr><td>(CS)<sub>2</sub>DEAEM</td><td></td></tr><tr><td>Structure determination</td><td></td></tr><tr><td>Ultraviolet spectra</td><td></td></tr></tbody></table>			O-Chlorobenzylidenemalononitrile	Infrared spectra	CS	Raman spectra	2-Diethylaminoethyl mercaptan	Benzylidenemalononitriles	DEAEM	NaCN	Reaction products	NaHSO <sub>3</sub>	CS(DEAEM) <sub>2</sub>	Pentanethiol	(CS) <sub>2</sub> DEAEM		Structure determination		Ultraviolet spectra	
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Chemical Research Division

June 1972

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Task 1B562602AD1002

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## FOREWORD

This work was conducted under Task 1B562602AD1002, Analytical Studies. The experimental data are contained essentially in notebooks 7326, 7396, and 7706 and in dated and signed spectra. The experimental work was started in June 1965 and completed in March 1968.

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## DIGEST

Ultraviolet, infrared, and Raman spectra have been determined for the products of the reaction of CS (*o*-chlorobenzylidenemalononitrile) and 2-diethylaminoethyl mercaptan (DEAEM). Structures for two of the products, CS(DEAEM)<sub>2</sub> and (CS)<sub>2</sub>DEAEM, are given, and their spectral characteristics are discussed. Reactions were followed in the ultraviolet by observing the changes occurring in the spectrum with time. Possible reaction mechanisms are discussed for the formation of the product CS(DEAEM)<sub>2</sub>. The order of addition of DEAEM to CS in the case of the product CS(DEAEM)<sub>2</sub>, as observed by ultraviolet, is first, the addition to the double bond, and second, addition to the nitrile.

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# SPECTROSCOPIC ANALYSIS OF THE PRODUCTS FROM THE REACTION OF *o*-CHLOROBENZYLIDENEMALONONITRILE (CS) AND 2-DIETHYLAMINOETHYL MERCAPTAN (DEAEM)

## I. INTRODUCTION.

The addition of mercaptan to active double bonds has been the basis for an analytical method<sup>1</sup> for acrylonitrile and  $\alpha,\beta$ -unsaturated carbonyl compounds. This addition is base catalyzed and results generally in the addition of one molecule of mercaptan, as in the case of acrylonitriles.<sup>1</sup> However, Sass et al.<sup>2</sup> reported the addition of more than one molecule of mercaptan in the base catalyzed reaction with CS (*o*-chlorobenzylidenemalononitrile) and related benzylidenemalononitriles. Holmes has reported on the spectral<sup>3,4</sup> and polarographic<sup>4</sup> analysis of some benzylidenemalononitriles and related compounds and on their rates of reaction with amines. Weir and Hyne have investigated the base-catalyzed dimerizations of several alkylidenemalononitriles,<sup>5</sup> and the base-catalyzed condensations of the systems  $\phi\text{CH}_2\text{C}=\text{C}(\text{CN})_2$ ,  $\phi\text{HC}=\text{C}(\text{CN})_2$ , and  $\text{CH}_3\text{HC}=\text{C}(\text{CN})_2$ .<sup>6</sup> Proton nuclear magnetic resonance spectral evidence was presented in support of the suggested cyclic structures of the dimerization and condensation products. The infrared<sup>7,8</sup> and Raman<sup>8</sup> spectra for a large number of benzylidenemalononitriles and related compounds have also been determined. Feniak, Holmes, and Reesor<sup>9</sup> studied the reaction of mercaptan with benzylidenemalononitriles in the presence of piperidine and proposed a reaction scheme. Tarantino and Sass<sup>10,11</sup> have made extensive studies on the reaction between benzylidenemalononitriles and 2-diethylaminoethyl mercaptan (DEAEM), using polarography to obtain reaction rates and reaction mechanisms. DEAEM was used because the molecule contains both the amine and mercaptan moieties and thus would simulate the protein-thiol present in vivo.

<sup>1</sup> Beesing, D. W., Tyler, W. P., Kurtz, D. M., and Harrison, S. A. Determination of Acrylonitrile and Alpha, Beta-Unsaturated Carbonyl Compounds Using Dodecanethiol. *Anal. Chem.* **21**, 1073 (1949).

<sup>2</sup> Sass, S., Davis, P. M., Master, I., Reynolds, R. A., Roberts, E., Sechrist, J., and Beitsch, N. CWLR 2396. Analytical Methods for CS. Part II. Volumetric Determination of CS Purity; Estimation of Total Volatiles in CS. May 1960. UNCLASSIFIED Report.

<sup>3</sup> Currie, D. J., Lough, C. E., Silver, R. F., Holmes, H. L. Functional Group and Substituent Effects. Both Spheric and Electronic, Upon the Ultraviolet Spectra of Some Conjugated Heteroenoid Compounds. *Can. J. Chem.* **45**, 1567-1580 (1967).

<sup>4</sup> Holmes, H. L. Suffield Technical Paper 231. A Theory for the Action of Benzalmalononitriles on Nerve Endings. Part III. Spectral and Polarographic Analysis of the Benzalmalononitriles and Related Compounds and Their Rates of Reaction with Amines. March 1962. UNCLASSIFIED Paper.

<sup>5</sup> Weir, M. R. S., and Hyne, J. B. Base-Catalyzed Dimerizations of Alkylidenemalononitriles. *Can. J. Chem.* **42**, 1440 (1964).

<sup>6</sup> Weir, M. R. S., and Hyne, J. B. Some Base-Catalyzed Condensations of Systems of the Form  $\text{R}_1\text{R}_2\text{C}=\text{C}(\text{CN})_2$ . *Can. J. Chem.* **43**, 772 (1965).

<sup>7</sup> Currie, D. J., Lough, C. E., McClusky, F. K., and Holmes, H. L. Suffield Special Publication 55. The Infrared Spectra of Some Conjugated Heteroenoid Compounds. February 1966. UNCLASSIFIED Report.

<sup>8</sup> Piffath, R. J., and Sass, S. EATR 4327. Infrared and Raman Spectra of Some Benzylidenemalononitriles, Cinnamylidenemalononitriles, Cinnamonnitriles, 3-Indoleacrylonitriles, and Related Compounds. November 1969. UNCLASSIFIED Report.

<sup>9</sup> Feniak, G., Holmes, H. L., and Reesor, J. B. Suffield Technical Paper 297. Reactions of Nucleophilic Agents with Irritant Compounds. Part I. Reaction of Nucleophilic Agents with Dibenzoxazepine, Acridine, and Benzalmalononitriles. May 1964. UNCLASSIFIED Paper.

<sup>10</sup> Tarantino, P. A., and Sass, S. EATR 4104. An Investigation of the Rates of Reaction of Benzalmalononitriles and Other Irritants with 2-Diethylaminoethyl Mercaptan (DEAEM), Employing Controlled Potential DC Polarography. I. Polarography and Rates of Reaction of DEAEM with CS. July 1967. UNCLASSIFIED Report.

<sup>11</sup> Tarantino, P. A., and Sass, S. EATR 4384. An Investigation of the Rates of Reaction of Benzalmalononitriles and Other Irritants with 2-Diethylaminoethyl Mercaptan (DEAEM), Employing Controlled Potential DC Polarography. III. Structure-Activity Relationships of Some Benzylidenemalononitriles. April 1970. UNCLASSIFIED Report.

Tarantino and Sass<sup>10</sup> have reported that the products formed in the reaction of CS and DEAEM depended on the concentration of the reactants. They reported the following conclusions based on various reactant ratios: (1) in a 1:1 reaction mixture, DEAEM added to the  $\alpha,\beta$ -double bond of CS produced initially a monothioether (CS-DEAEM); (2) with CS in excess, the same product formed. After long standing (hours to days), a product formed in both reaction mixtures that had the empirical formula  $(CS)_2$  DEAEM. (3) With DEAEM in excess, a product formed having the empirical formula  $CS(DEAEM)_2$ , through addition of the DEAEM first to the  $\alpha,\beta$ -double bond and then to a nitrile of CS. This report describes the results of the ultraviolet (UV), infrared (IR), and Raman spectroscopic studies of the reaction products of CS and DEAEM, namely  $CS(DEAEM)_2$  and  $(CS)_2$  DEAEM.

## II. EXPERIMENTATION.

### A. Reagents.

1. 2-Diethylaminoethyl mercaptan (DEAEM). Purification is given by Tarantino and Sass.<sup>10</sup>
2. *o*-Chlorobenzylidenemalononitrile (CS), 99%.
3. Methanol, reagent grade, Allied Chemical.
4. Sodium cyanide, reagent grade, Mallinckrodt.
5. Sodium bisulfite, reagent grade, J. T. Baker.
6. 1-Pentanethiol, reagent grade, Eastman Organic Chemicals.
7. Chloroform, infrared quality, Matheson Coleman and Bell.

### B. Instrumentation.

#### 1. Ultraviolet Spectra and Procedure.

Ultraviolet spectra were determined on a Cary 14 recording spectrophotometer\* using 1.0-, 0.2-, and 0.1-cm silica cells. The UV spectra of specific compounds were run on approximately  $5 \times 10^{-4}$  M methanol, chloroform, and methylene chloride solutions.

Reactions were followed, in the UV, by adding the particular reagent to a solution of CS, placing the reaction solution as quickly as possible into a cell, and then scanning the spectrum several times over a period of time.

#### 2. Infrared Spectra.

Infrared spectra were determined on a Perkin-Elmer 521 grating spectrophotometer. Solid samples were run as potassium bromide pellets using infrared quality KBr (Harshaw Chemical Company, Cleveland, Ohio). Spectra also were recorded for chloroform solutions. Liquids were run as capillary films between KBr windows. Deuteration studies were performed with  $D_2O$ , 99.5 mol % min (Matheson Coleman and Bell). A few drops of  $D_2O$  were added to a solution of the sample in chloroform. After shaking and phase separation, the chloroform layer was removed; then the infrared spectrum was run against a blank composed of chloroform containing a few drops of  $D_2O$ .

\*Cary Instruments, Monrovia, California.

### 3. Raman Spectra.

Raman spectra were recorded on a Cary 81 spectrophotometer\* equipped with a 50-mW Spectra-Physics model 125 CW He/Ne gas laser source,\*\* using the 6328Å laser line for excitation and the 180° viewing technique.

The Raman solid sample holder rod has a concave conical face, and the sample is held in position by compaction. The sample holder rod, conical end down, was placed in a vial containing the powdered sample. The rod was tamped down gently several times into the powder, with rotation, causing the sample to be compacted into the conical hole. The excess sample was wiped off the outside surface of the rod; the rod was clamped in the solid sample holder and placed in the sample compartment of the instrument.

Raman spectra of liquid samples were obtained with a fused silica capillary cell 6 cm in length, 1-mm OD and 0.6-mm ID, with a window at one end and a capacity of 25  $\mu$ l. The cell, while in its holder, was filled with a 0.25-ml hypodermic syringe with a 27-gage by 10-cm-long blunt hypodermic needle. A small drop of glycerol was applied to the open end of the cell to prevent evaporation of volatile samples. Another drop of glycerol was applied to the window end of the cell to improve optical efficiency. The sample holder and cell were then placed in the sample compartment of the spectrophotometer.

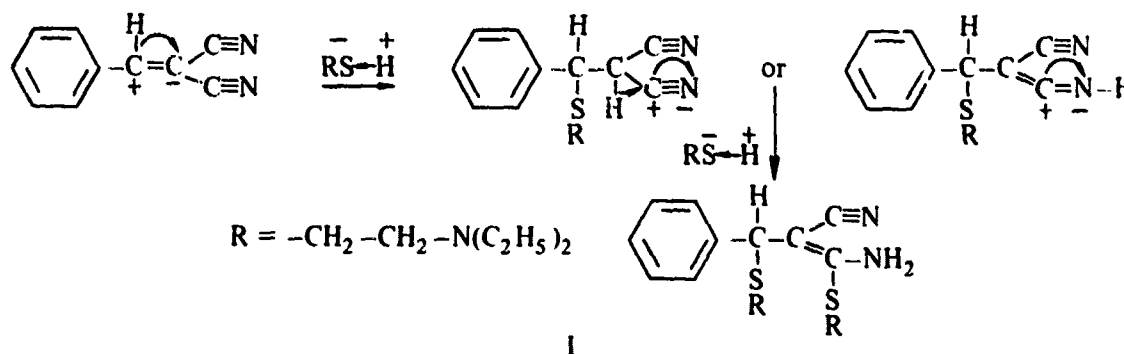
### III. RESULTS AND DISCUSSION.

The ultraviolet, infrared, and Raman spectra of the products from the reaction of CS and DEAEM are reproduced in the appendix.

#### A. Ultraviolet Spectral Data.

Spectra were obtained on two isolated solid products from the reaction of CS with DEAEM. One was a product empirically representing 2 CS to 1 DEAEM, and the other 1 CS to 2 DEAEM. In addition, spectra were obtained for the reaction products as they formed in solution. As these products were not isolated from solution, their spectral data,  $\lambda_{max}$  and  $\epsilon_{max}$ , were taken at maximum absorption and are given in table I. In addition to the spectra of the reaction products of CS with DEAEM, spectra also were obtained for the products of the reaction of CS with pentanethiol, sodium cyanide, and sodium bisulfite and the subsequent reaction of these latter products with DEAEM.

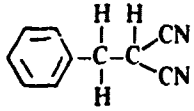
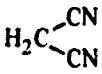
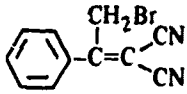
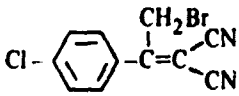
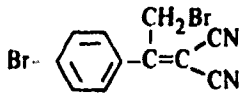
The mechanism for the formation of the product in the reaction of two moles of mercaptan with benzyldienemalononitriles has been postulated<sup>10</sup> as follows:



\*Ibid.

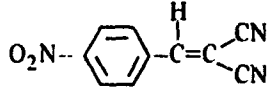
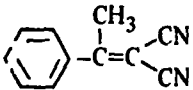
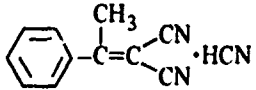
\*\*Spectra-Physics, Inc, Mountain View, California.

Table I. UV Spectral Maxima of CS and CS Analogs and Their Reaction Products With Various Nucleophiles

Original compound	Reactant	Spectral maxima			
		Original compounds		Products	
		$\lambda_{\max}$	$\epsilon_{\max}$	$\lambda_{\max}$	$\epsilon_{\max}$
CS(DEAEM) <sub>2</sub>		<i>nm</i> 292	16,100	<i>nm</i>	
(CS) <sub>2</sub> DEAEM		285 277 sh 270 sh 214 inf	15,000 14,200 12,200 25,300		
CS	DEAEM in excess	299	15,000	291	15,400
CS	NaCN	299	15,000	268	566
CS·HCN	DEAEM	268	566	285	16,000
CS	NaHSO <sub>3</sub>	299	15,000	277 269	620
CS·HSO <sub>3</sub>	DEAEM	277 269	620	288	16,200
CS	C <sub>5</sub> H <sub>11</sub> SH (large excess)	299	15,000	298*	1,550
CS·C <sub>5</sub> H <sub>11</sub> SH	DEAEM	298*	1,550	289	16,900
	DEAEM	258	200	280	15,000
	DEAEM	—	—	270	14,400
	DEAEM	306	11,000	288	13,000
	DEAEM	312	12,200	293	14,300
	DEAEM	311	12,900	295	15,300

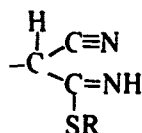
\*90% of CS reacted.

Table I. Continued

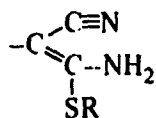
Original compound	Reactant	Spectral maxima			
		Original compounds		Products	
		$\lambda_{\max}$	$\epsilon_{\max}$	$\lambda_{\max}$	$\epsilon_{\max}$
	DEAEM	<i>nm</i> 305	19,700	<i>nm</i> 280	21,400
	NaCN	289	13,200	258	540
	DEAEM	258	540	282	9,670

The IR data, which will be discussed later, are consistent with the structure of the final product (I), and the rates of addition have been followed polarographically.<sup>10,11</sup> The spectrum, in solution, of the final reaction product of CS with a five- or tenfold excess of DEAEM is the same as for I, namely CS(DEAEM)<sub>2</sub>. Attempts to stop the reaction after the addition of one mole of DEAEM to CS were unsuccessful because the initial reaction is too fast, leading rapidly to an equilibrium mixture of mono- and diadduct.

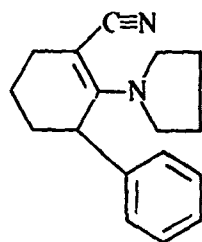
One way to isolate or simulate the equivalent addition of the second mole of DEAEM to CS or an analog is to add the DEAEM after the elimination of the double bond. The double bond is absent or has been eliminated in a compound such as benzylmalononitrile and in the reaction products of CS with sodium cyanide, sodium bisulfite, and pentanethiol. Each of these compounds showed a UV spectrum like that of an isolated phenyl group (250- to 270-nm region) before reaction with DEAEM. But on the addition of DEAEM to the solution, an intense peak developed in the 280- to 290-nm region with an  $\epsilon_{\max}$  around 15,000. These experiments indicate that the order of addition, as observed by UV, is initially to the double bond, followed by a further addition to the nitrile. These results are in agreement with the mechanism given above.<sup>10</sup> Addition of DEAEM only to the nitrile, however, would result in a nonconjugated product that would absorb weakly in the UV, having a structure:



The high intensity described above requires conjugation, and this is produced by the proton shift resulting in the structure:

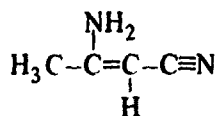


$\alpha,\beta$ -Unsaturated nitriles<sup>12</sup> have their main peak around 215 nm,  $\epsilon_{\text{max}}$  10,000. The large bathochromic shift in the CS-DEAEM products must be caused by the amine and sulfide groups. Spectra of enamines conjugated to nitriles have been reported with intense bands above 250 nm in compounds II<sup>13</sup> and III.<sup>14,15</sup>



II

$\lambda_{\text{max}}$  289 nm  
 $\epsilon_{\text{max}}$  17,500

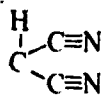


III

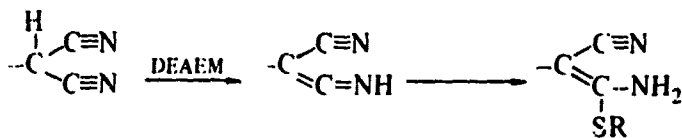
$\lambda_{\text{max}}$  258 nm  
 $\epsilon_{\text{max}}$  19,000

The exact contribution of the sulfide group is not known, but increases in peak intensities occur in  $\alpha,\beta$ -unsaturated sulfides. Allyl sulfide<sup>16</sup> has a  $\lambda_{\text{max}}$  at 221 nm and  $\epsilon_{\text{max}}$  of 2000, whereas methyl vinyl sulfide<sup>17</sup> has a  $\lambda_{\text{max}}$  at 240 (sh) and 225 nm with  $\epsilon_{\text{max}}$  of 10,000 and 15,850 respectively. The variation in the  $\lambda_{\text{max}}$  of the different reaction products of CS with DEAEM must be a result of the influence of the remaining group, even if it is not conjugated to the chromophore.

These experiments also indicate that the double bond is not necessary for the reaction that produces the chromophore, but only the



group is required. The UV and IR spectra do not indicate the presence of ketenimine before the reaction, as postulated by Holmes<sup>3</sup> and Tarantino and Sass,<sup>10</sup> but the ketenimine might be induced by the presence of DEAEM before its reaction to form the addition product.



<sup>12</sup>Schenker, K., and Druey, J. Chemotherapeutic Studies in the Heterocyclic Series. XXV. Hydropyridines. I. Reduction of 1-Methyl-3-cyanopyridinium Iodide with Sodium Borohydride. *Helv. Chim. Acta* 42, 1960 (1959). In German. *CA* 54, 9912e, 12133h.

<sup>13</sup>Baldwin, S. J. Infrared and Ultraviolet Absorption Spectra of Enaminonitriles. *J. Org. Chem.* 26, 3288 (1961).

<sup>14</sup>Middleton, W. J., and Engelhardt, V. A. Cyanocarbon Chemistry. IV. Dicyanoketene Acetals. *J. Amer. Chem. Soc.* 80, 2788 (1958).

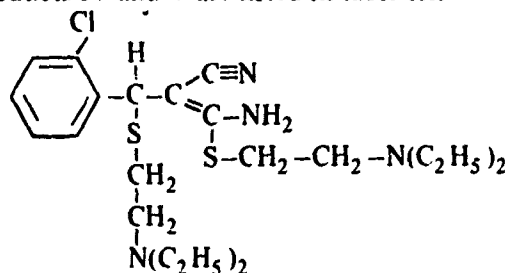
<sup>15</sup>Kurtz, P., Gold, H., and Disselhotter, H. Nitrile Formation. III. 1-Cyano-2-alkynes and 1-Cyano-1,2-alkadienes. *Justus Liebigs Ann. Chem.* 624, 1 (1950). In German. *CA* 54, 274f.

<sup>16</sup>Fehnel, E. A., and Carmall, M. The Ultraviolet Absorption Spectra of Organic Sulfur Compounds. I. Compounds Containing the Sulfide Function. *J. Amer. Chem. Soc.* 71, 84 (1949).

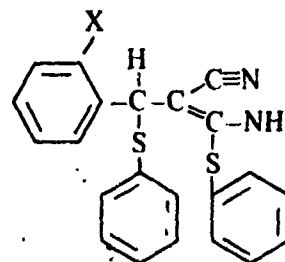
<sup>17</sup>Price, C. C., and Morita, H. Copolymerization Characteristics and Spectra of Phenyl Vinyl Sulfide and Sulfone. *J. Amer. Chem. Soc.* 75, 4747 (1953).

## B. Infrared and Raman Spectral Data for $\text{CS}(\text{DEAEM})_2$ and $(\text{CS})_2\text{DEAEM}$ .

As stated previously, two of the products formed in the reaction of CS and DEAEM have the empirical formulas  $\text{CS}(\text{DEAEM})_2$  and  $(\text{CS})_2\text{DEAEM}$ . The product  $\text{CS}(\text{DEAEM})_2$  has structure I and is similar to the product (IV)\* formed in the reaction of benzyldenemalononitrile with phenyl mercaptan, and the product (V)\*\* formed in the reaction of CS with phenyl mercaptan, as done in these laboratories. Infrared and Raman data for product I are listed in table II, and infrared data for products IV and V are listed in table III.



I



IV, X = H  
V, X = Cl

Products I, IV, and V all show an intense  $\nu\text{C}\equiv\text{N}$  band between 2200 and 2180  $\text{cm}^{-1}$  and a strong band around 1540  $\text{cm}^{-1}$  resulting from the olefinic  $\text{C}=\text{C}$  stretch. The attachment of a sulfur atom to the olefinic double bond, together with the conjugation of the olefinic double bond with the nitrile, usually lowers and intensifies the  $\nu\text{C}=\text{C}$  band.<sup>18</sup> Two or three bands are observed in the NH stretching region. For product I in chloroform, the  $\nu\text{NH}_2$  bands occur at 3423 and 3270  $\text{cm}^{-1}$  and shift to 2550 and 2440  $\text{cm}^{-1}$  on deuteration. The 2900  $\text{cm}^{-1}$  region also changes on deuteration, and a band appears at ca 2200  $\text{cm}^{-1}$ , which indicates that a  $\nu\text{NH}$  band also occurs in the CH stretching region (2900  $\text{cm}^{-1}$ ) and overlaps the normal CH stretching bands. The band is probably caused by an N-H (of the  $\text{NH}_2$  group) bonded to the N in the amine moiety of the mercaptan. This band does not occur in IV and V because the phenyl mercaptan does not contain an amine moiety; thus, this type of hydrogen bonding is precluded. The 1637  $\text{cm}^{-1}$  band also shifts on deuteration, indicating that this band is a result of the  $\delta\text{NH}_2$ . The low nitrile stretching band observed for products I, IV, and V is caused by the presence of the unsaturated  $\beta$ -amino group and can be explained in terms of the enaminonitrile structure ( $\text{H}_2\text{N}-\text{C}=\text{C}-\text{C}\equiv\text{N}$ ), which absorbs strongly at 2210 to 2185  $\text{cm}^{-1}$  due to resonance ( $\text{>}\ddot{\text{N}}=\text{CH}-\text{CH}=\text{C}=\ddot{\text{N}}$ ).<sup>13</sup>

*Anal* for I as  $\text{C}_{22}\text{H}_{35}\text{N}_4\text{S}_2\text{Cl}$ . Calcd: C, 58.06; H, 7.8; N, 12.3; S, 14.1; Cl, 7.79. Found: C, 58.10; H, 7.6; N, 12.6; S, 14.4; Cl, 7.78.

The product  $(\text{CS})_2\text{DEAEM}$  presents a more complicated problem. *Anal* for  $(\text{CS})_2\text{DEAEM}$  as  $\text{C}_{26}\text{H}_{25}\text{N}_5\text{SCl}_2$ . Calcd: C, 61.2; H, 4.9; N, 13.7; S, 6.3; Cl, 13.9. Found: C, 60.6; H, 4.8; N, 14.0; S, 6.4; Cl, 13.9.

The IR and Raman spectral data for  $(\text{CS})_2\text{DEAEM}$  are listed in table IV. No NH stretching band is observed in the normal area for  $(\text{CS})_2\text{DEAEM}$ . A broad band occurs in the range 3300 to 2000  $\text{cm}^{-1}$  in KBr and  $\text{CHCl}_3$ , having its center at ca 2660  $\text{cm}^{-1}$ . A strong band occurs at 2198  $\text{cm}^{-1}$  in  $\text{CHCl}_3$  (2195  $\text{cm}^{-1}$  in KBr and 2192  $\text{cm}^{-1}$  in the Raman) and is assigned to a  $\nu\text{C}\equiv\text{N}$ .

\*Sample isolated by R. Proper, Organic Chemistry Department. Anal. 9912.

\*\*Sample obtained from Suffield Experimental Station, Ralston, Alberta.

<sup>18</sup>Colthup, N. B., Daly, L. H., and Wiberley, S. E. Introduction to Infrared and Raman Spectroscopy. p 211. Academic Press, New York, New York, 1964.

Table II. Infrared and Raman Data for CS(DEAEM)<sub>2</sub>

IR (KBr)	Raman (solid)	IR (CHCl <sub>3</sub> )*	Assignment
<i>cm<sup>-1</sup></i>			
—	—	3423 VW	νNH <sub>2</sub>
3230 W	—	ca 3270 VW	
ca 3190 W	—	—	
ca 2900 B	—	ca 2900 B	
ca 3068 VVW	3068 VVW	—	νCH aromatic
ca 3055 VVW	ca 3059 VVW	—	
2973 MS	2964 VW	2976 S	ν <sub>as</sub> and ν <sub>sy</sub> CH <sub>3</sub> ,CH <sub>2</sub>
2936 M	ca 2935 VVW	2938 M	
2923 M	2923 W	—	
2876 W	2868 VVW	2879 VW	
2831 MS	ca 2835 VVW	2823 M	
2808 W	—	—	
2180 S	2176 S	2186 MS	νC≡N (conjugated)
ca 1668 W	—	ca 1637 W	δNH <sub>2</sub>
1590 VVW	1591 M	1592 VVW	Aromatic ring C=C
1571 VW	1574 W	ca 1571 sh	
1534 S	1538 MS	1540 S	νC=C olefinic (conjugated)
1469 sh	—	1467 M	Various deformations of N-CH <sub>2</sub> , S-CH <sub>2</sub> ,CH <sub>3</sub>
1463 M	1459 W	—	
1450 W	1453 W	1450 W	
1438 W	—	—	
1426 sh	1427 VW	—	
1406 W	1406 VVW	1407 VW	
1380 M	1378 VW	1388 W	
1374 W	—	1377 W	
1288 M	1289 VW	1291 W	Vibrations of the mercaptan moiety
1194 M	1202 VW	1191 W	
1180 sh	1181 MS	—	βCH <i>ortho</i> substitution
1030 M	1032 MS	1032 W	
753 M	—	—	γCH <i>ortho</i> substitution
740 M	743 M	—	
666 VVW	668 MS	—	νC-S

\*The product CS(DEAEM)<sub>2</sub> appears to dissociate in CHCl<sub>3</sub> as bands appear at 2235 and 1592 cm<sup>-1</sup>. The bands probably are caused by CS.



Table III. Infrared Data for Products IV and V in KBr

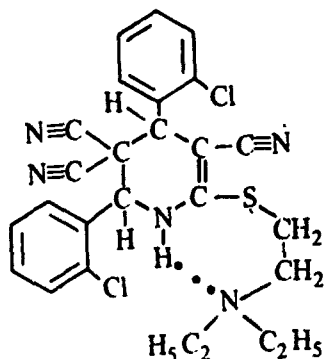
IV	V	Assignment
<i>cm<sup>-1</sup></i>		
3465 W	3464 MS	$\nu\text{NH}_2$
3324 M	3362 S	
3219 W	3187 VW	
ca 3070 sh	ca 3073 sh	$\nu\text{CH aromatic}$
ca 3060 VW	3062 W	
ca 3030 VVW	—	
ca 3020 sh	3019 VVW	
2191 MS	2188 MS	$\nu\text{C}\equiv\text{N}$
1622 S	1605 S	$\delta\text{NH}_2$
ca 1600 sh	—	Aromatic ring C=C
ca 1590 inf	1582 VW	
ca 1575 inf	1571 VW	
1497 VW	1480 M	
1473 W	1471 MS	
1453 W	—	
1438 W	1439 MS	
1560 M	—	$\nu\text{C}=\text{C olefinic (conjugated)}$
1545 sh	1544 S	
1301 VW	1306 M	$\nu\text{C}-\text{N}?$
1068 VW	1070 W	$\beta\text{CH aromatic rings}$
—	1054 sh	
—	1048 W	
—	1033 W-M	
1024 W	1026 M	
1002 VW	1002 W	$\gamma\text{CH aromatic rings}$
752 M	751 S	
703 M	699 sh	
691 M	694 MS	

Because of its intensity and low position, the nitrile band must be conjugated and similar to the type found in  $\text{CS}(\text{DEAEM})_2$ , namely a  $\beta$ -amino unsaturated nitrile. A very weak band occurs at ca  $2253\text{ cm}^{-1}$  in  $\text{CHCl}_3$  and KBr and at  $2249\text{ cm}^{-1}$  (W) in the Raman. This band can be assigned to a saturated nitrile. A strong band occurs at ca  $1545\text{ cm}^{-1}$  (KBr),  $1537\text{ cm}^{-1}$  (Raman), which is assigned to a conjugated olefinic  $\nu\text{C}=\text{C}$ . A sulfur atom is probably attached to the  $\text{C}=\text{C}$  group, as this together with conjugation usually lowers and intensifies the  $\nu\text{C}=\text{C}$ .<sup>18</sup> The broad band observed between  $3300$  and  $2000\text{ cm}^{-1}$  did not change in intensity on dilution in  $\text{CHCl}_3$ , but the band center ( $2660\text{ cm}^{-1}$ ) shifted to the  $2000\text{ cm}^{-1}$  area on deuteration. A change also occurred in the  $1550\text{ cm}^{-1}$  area on deuteration. This would indicate an NH group that is intramolecularly hydrogen bonded. The hydrogen bond is also quite strong judging from its low position, perhaps because of a  $\text{N}-\text{H}\cdots\text{N}$  hydrogen bond.

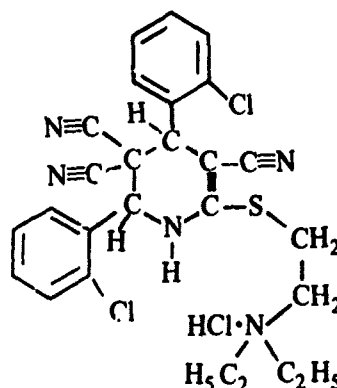
Table IV. Infrared and Raman Data for (CS)<sub>2</sub>DEAEM

IR, KBr	IR, CHCl <sub>3</sub>	Raman (solid)	Assignment
<i>cm</i> <sup>-1</sup>		$\Delta cm^{-1}$	
ca 3067 VW ca 3020 VVW	ca 3064 VW ca 3025 VW	ca 3065 VW —	$\nu$ CH aromatic
ca 2978 M ca 2940 W ca 2880 VW ca 2832 VW	ca 2980 M ca 2941 W ca 2880 VW ca 2836 W	ca 2976 VVW ca 2935 VW — —	$\nu_{as}CH_3$ $\nu_{as}CH_2$ $\nu_{sy}CH_3$ $\nu_{sy}CH_2$
ca 2660 B	ca 2660 B	—	$\nu$ NH bonded; shifts to 2000 <i>cm</i> <sup>-1</sup> area on deuteration
ca 2250 VVW 2195 S	ca 2253 VVW 2198 S	2249 VW 2192 S	$\nu C\equiv N$ saturated $\nu C\equiv N$ conjugated
ca 1590 inf — ca 1577 sh	ca 1591 sh — 1577 sh	1596 W 1588 W 1566 W	Aromatic ring C=C
1545 S	1548 S	1537 M	$\nu C=C$ olefinic, $\delta$ NH could also absorb here
1474 M	1475 M	—	$\delta CH_3, CH_2$
1450 sh	1450 M	1454 W	Aromatic ring C=C
1440 M 1409 W 1378 W	1440 sh 1410 W 1380 W	— 1406 1376 VW	$\delta S-CH_2?$ $\delta_{sy}CH_3?$
1285 M	1284 M	1285 W	$\omega S-CH_2?$
1190 W —	1190 W —	1188 M 1039 M	$\beta$ CH <i>ortho</i> -subs(?) $\beta$ CH <i>ortho</i> -subs
755 MS	—	—	$\gamma$ CH <i>ortho</i> -subs
667 VW 653 sh	— —	667 M 654 M	$\nu C-S$

The hydrochloride salt of  $(CS)_2$ DEAEM analyzed as  $C_{26}H_{26}N_5SCl_3$  (Calcd: C, 57.10; H, 4.8; N, 12.8; S, 5.9; Cl, 19.4. Found: C, 57.17; H, 4.6; N, 12.8; S, 5.6; Cl, 19.3), showed bands at  $2600\text{ cm}^{-1}$  resulting from the  $\nu NH^+$  and a band at  $ca\ 3130\text{ cm}^{-1}$  (KBr) resulting from  $\nu NH$ . The  $\nu NH$  of the salt occurs higher than that of the free base ( $ca\ 2660\text{ cm}^{-1}$ ), indicating a weaker hydrogen bond in the salt. A  $N-H \dots N$  hydrogen bond would be quite strong, thus its lower position in the free base. In the salt, the tertiary nitrogen of the amino-mercaptan moiety would become blocked on salt formation, preventing the formation of the intramolecular  $N-H \dots N$  hydrogen bond. This would result in a weaker hydrogen bond (possibly intermolecular) as indicated by the higher frequency for the  $\nu NH$  in the salt than in the free base. The  $\nu C\equiv N$  of the hydrochloride salt occurs at  $2196\text{ cm}^{-1}$  (MS) and  $2250\text{ cm}^{-1}$  (VW) in KBr and at  $2193\text{ cm}^{-1}$  (S) and  $2250\text{ cm}^{-1}$  (W) in the Raman. The lower  $\nu C\equiv N$  band is probably caused by an enaminonitrile<sup>13</sup> moiety, whereas the higher  $\nu C\equiv N$  band would indicate a saturated nitrile moiety based on its position and intensity. Kitson and Griffith<sup>19</sup> have shown that saturated nitriles have their nitrile stretching band at  $2250 \pm 10\text{ cm}^{-1}$ . After the above data for both the free base and the hydrochloride salt of  $(CS)_2$ DEAEM were considered, structures VI and VII appear to best fit the infrared and Raman spectral data.



VI, Free Base of  $(CS)_2$ DEAEM



VII, HCl Salt of  $(CS)_2$ DEAEM

The UV bands for  $(CS)_2$ DEAEM are given in table I. The main peak at  $285\text{ nm}$ ,  $\epsilon_{max}$  15,000, can be attributed to the enamine structure conjugated to the nitrile. The peaks at  $277$  and  $270\text{ nm}$  may be only "shoulders" on the main peak caused by the isolated phenyl groups. The isolated chloro-phenyl group has  $\lambda_{max}$  at  $275$ ,  $268$ , and  $263\text{ nm}$ . Using baseline techniques, the  $\epsilon_{max}$  at  $277$  and  $270\text{ nm}$  were calculated to be about 500, which is what one would expect. The UV spectrum is consistent with the postulated structure (VI).

As stated previously, no indication of the ketenimine moiety,  $>C=C=N-$ , could be found in the ultraviolet or infrared spectra of the reaction products of CS and DEAEM. Ketenimines trisubstituted with aliphatic or aromatic groups absorb strongly at  $2050$  to  $2000\text{ cm}^{-1}$ .<sup>20</sup> No infrared band was ever observed in this region to indicate the presence of the ketenimine moiety. When CS and DEAEM were mixed together in various ratios in chloroform, and the reaction followed in the infrared, a band appeared at  $ca\ 2200\text{ cm}^{-1}$  or slightly below, indicating the presence of the enaminonitrile moiety,  $H_2N-C=C-C\equiv N$ . No band was observed in the  $2050$  to  $2000\text{ cm}^{-1}$  region.

<sup>19</sup>Kitson, R. E., and Griffith, N. E. Infrared Absorption Band Due to Nitrile Stretching Vibration. Anal. Chem. 24, 334 (1952).

<sup>20</sup>Stevens, L. C., and French, J. C. Nitrogen Analogs of Ketenes. II. Dehydrochlorination of Imino Chlorides. J. Amer. Chem. Soc. 76, 4398 (1954).

#### IV. CONCLUSIONS.

In the reaction of CS with diethylaminoethyl mercaptan (DEAEM), two products were formed having the empirical formulas  $\text{CS(DEAEM)}_2$  and  $(\text{CS})_2\text{DEAEM}$ . The former product formed with DEAEM in excess, and the latter product formed in a 1:1 reactant mixture after long standing. Structures have been postulated for both products based on their ultraviolet, infrared, and Raman spectra. The order of addition of DEAEM to CS in the case of the product  $\text{CS(DEAEM)}_2$ , as observed by ultraviolet, was first, addition to the double bond and second, addition to the nitrile.

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# APPENDIX

## UV SPECTRA

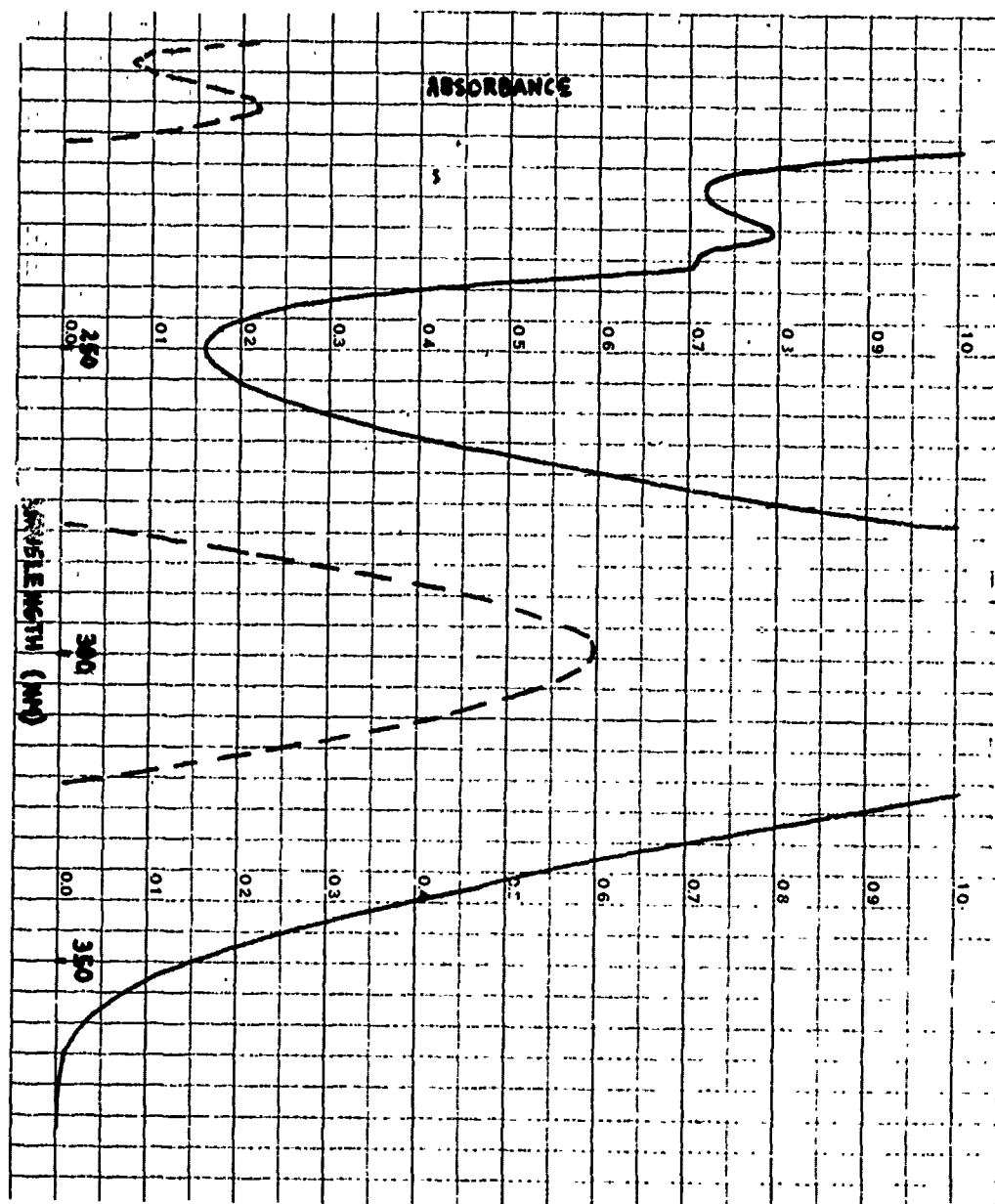


Figure A-1. *o*-Chlorobenzylidenemalononitrile (CS), 199  $\mu\text{g/ml}$ , 0.1 cm, in Methanol

In figures A-1 through A-25:

- absorbance 0 to 1
- - - absorbance 1 to 2

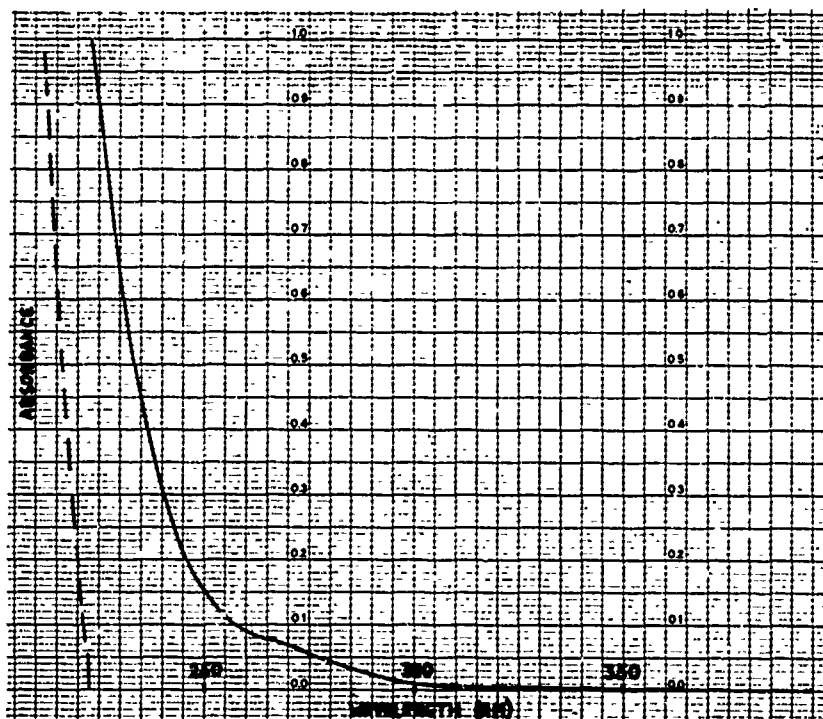


Figure A-2. 2-Diethylaminoethyl Mercaptan (DEAEM), 1500  $\mu\text{g/ml}$ , 0.1 cm, in Methanol

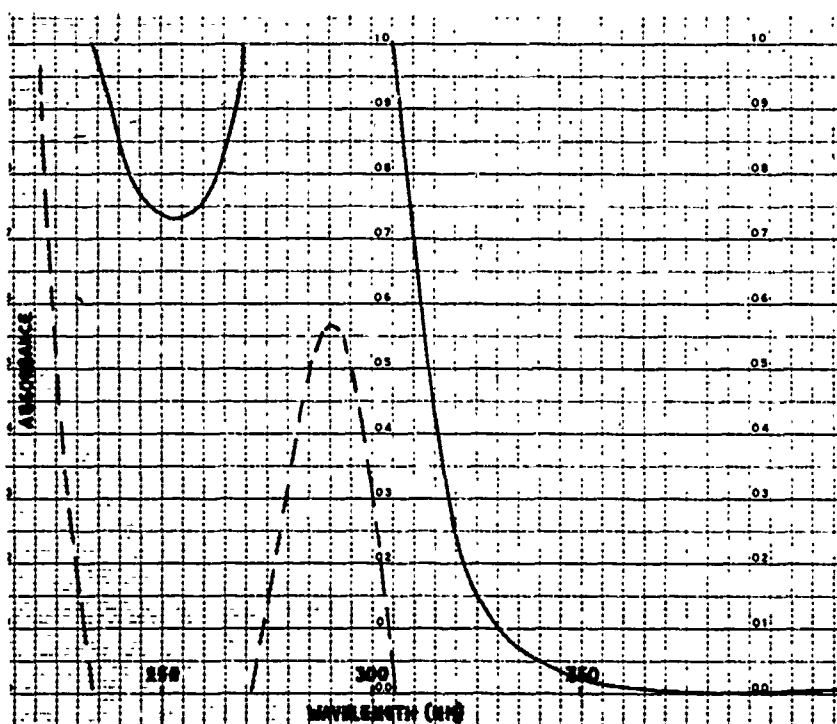


Figure A-3. CS + DEAEM in Excess, 19.7  $\mu\text{g/ml}$ , 1.0 cm, in Methanol



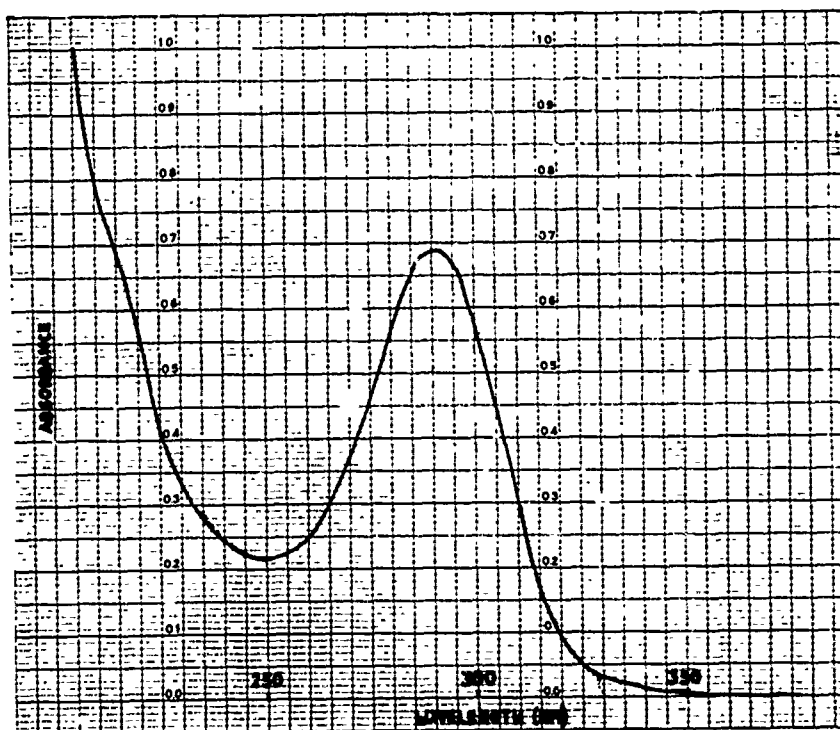


Figure A-4. CS(DEAEM)<sub>2</sub>, 192  $\mu\text{g/ml}$ , 0.1 cm, in Methanol

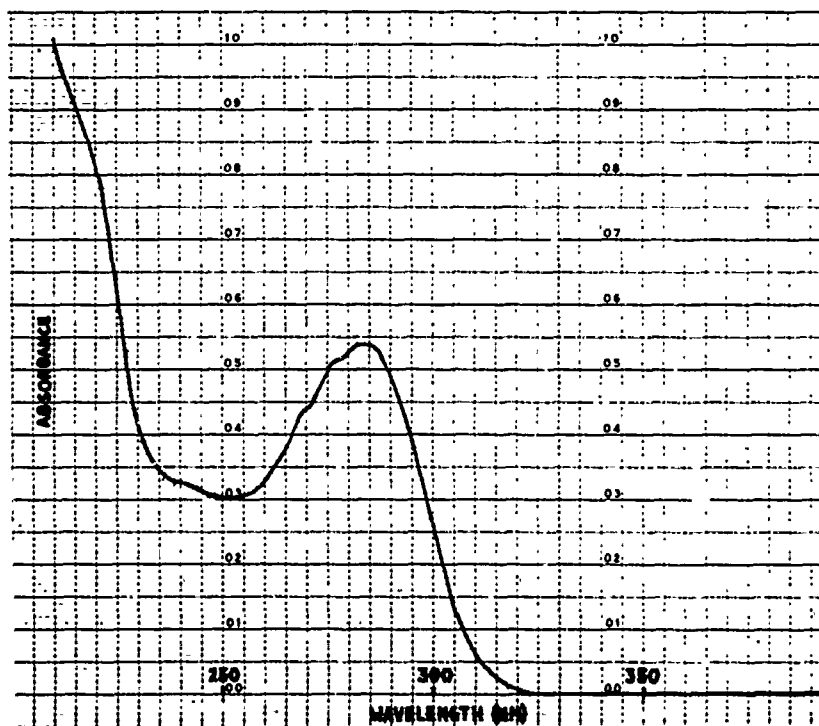


Figure A-5. (CS)<sub>2</sub>DEAEM, 92  $\mu\text{g/ml}$ , 0.2 cm, in Methanol

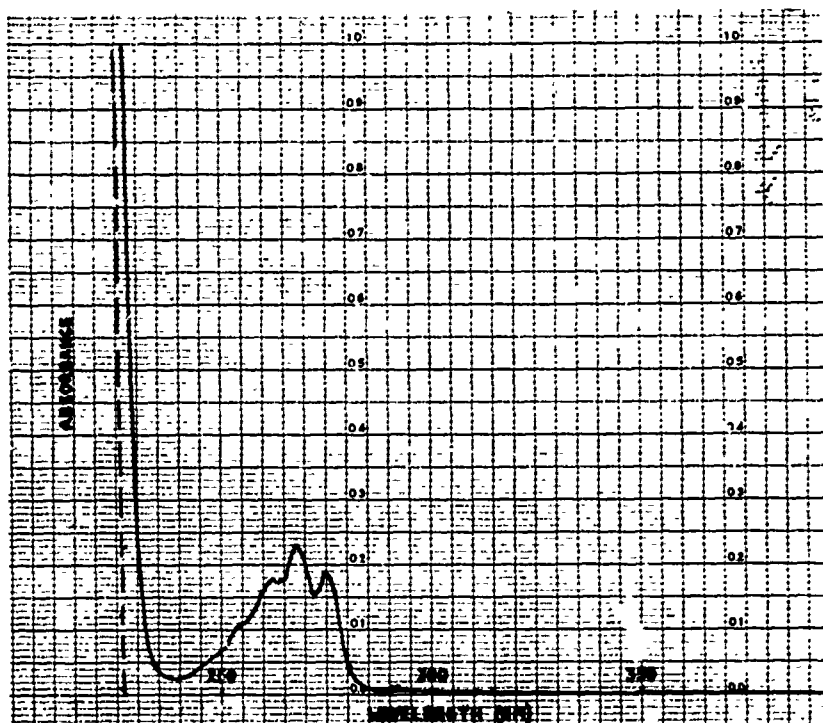


Figure A-6. CS + NaCN, 95.6  $\mu\text{g/ml}$ , 1.0 cm, in Methanol-Water

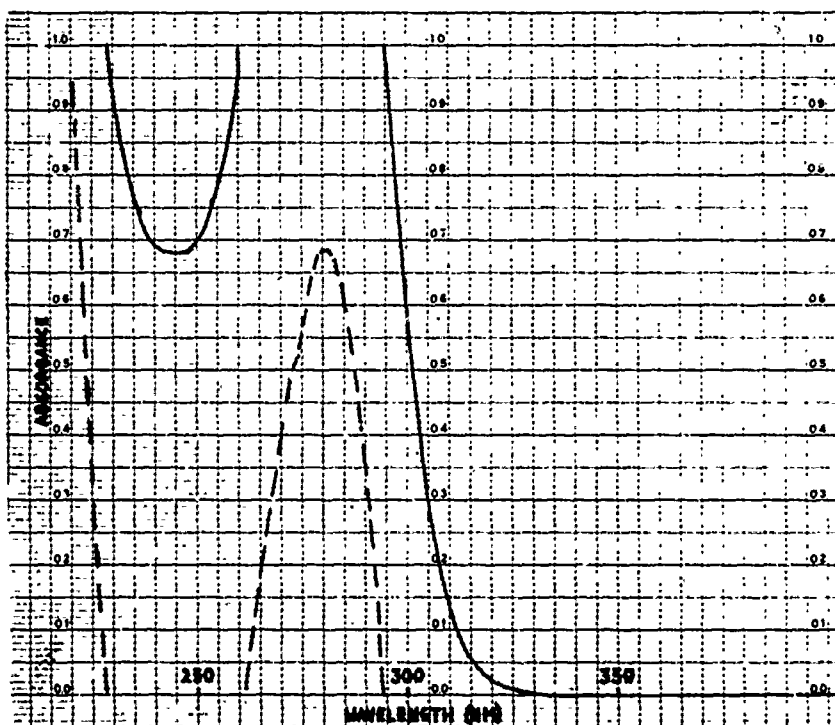


Figure A-7. CS + NaCN + DEAEM, 99.4  $\mu\text{g/ml}$  CS, 0.2 cm, in Methanol-1% Acetic acid

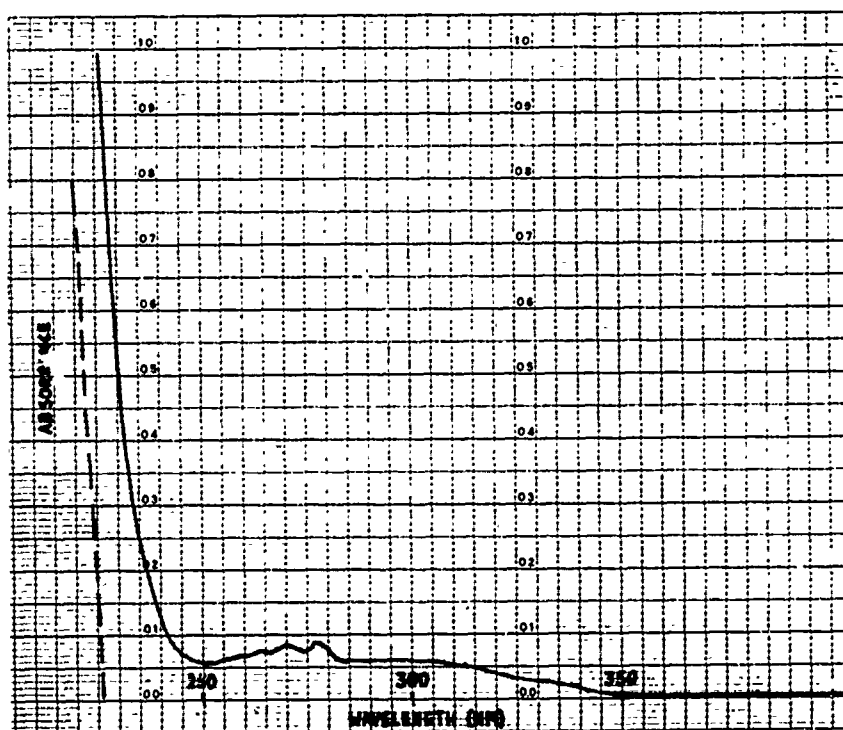


Figure A-8. CS + NaHSO<sub>3</sub>, 88.9 µg/ml CS, 0.2 cm,  
in Methanol-1% Acetic acid

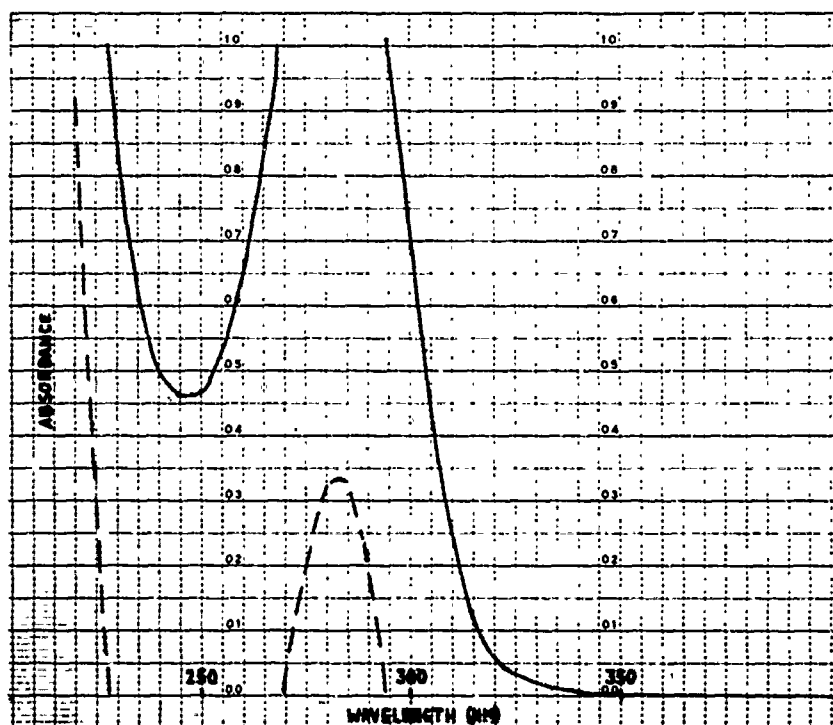


Figure A-9. CS + NaHSO<sub>3</sub> + DEAEM, 88.9 µg/ml CS, 0.2 cm,  
in Methanol-1% Acetic acid

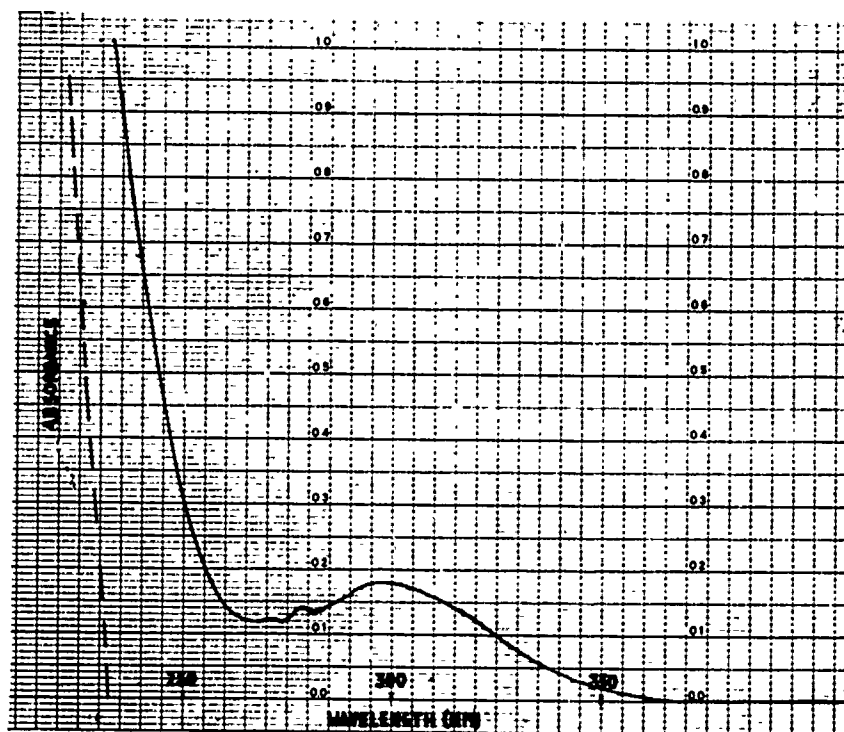


Figure A-10. CS +  $C_5H_{11}SH$  (1-Pentanethiol), 109.2  $\mu\text{g/ml}$  CS, 0.2 cm, in Methanol

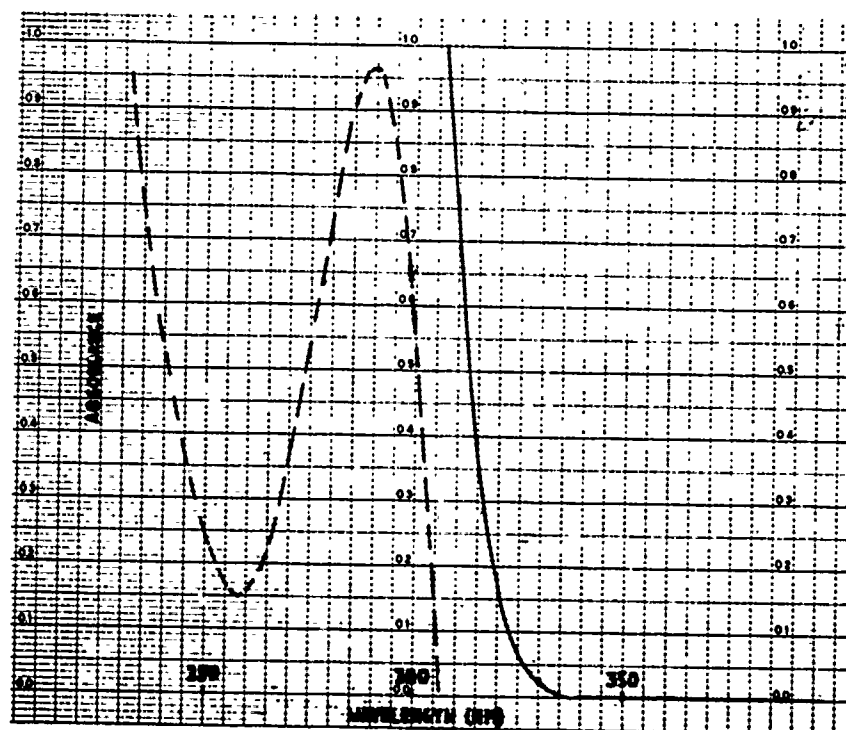


Figure A-11. CS +  $C_5H_{11}SH$  + DEAEM, 109.2  $\mu\text{g/ml}$  CS, 0.2 cm, in Methanol

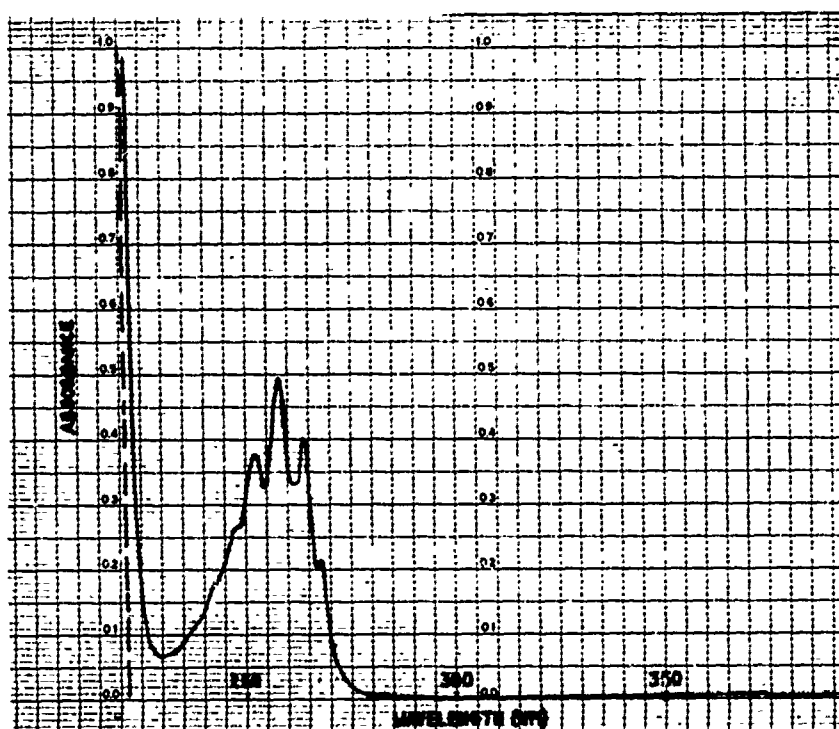


Figure A-12. Benzylmalononitrile, 403  $\mu\text{g/ml}$ , 1.0 cm, in Methanol

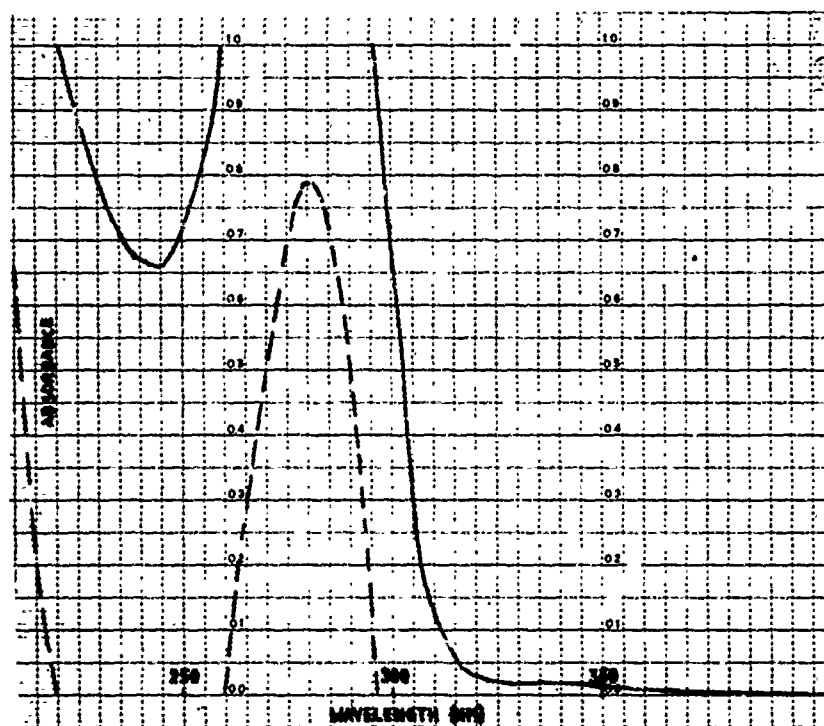


Figure A-13. Benzylmalononitrile + DEAEM, 18.5  $\mu\text{g/ml}$ , 1.0 cm, in Methanol

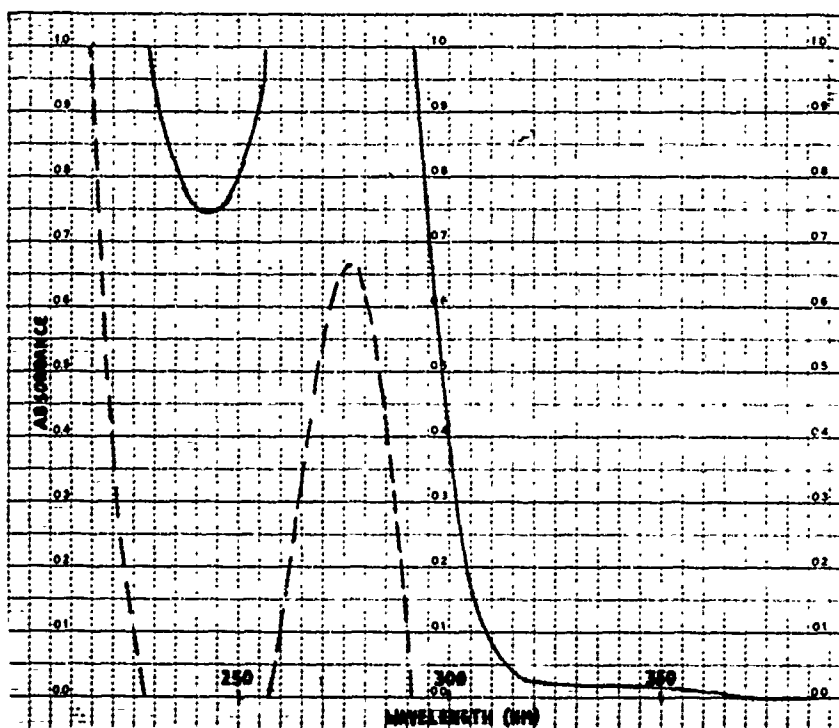


Figure A-14. Malononitrile + DEAEM, 38.0  $\mu\text{g/ml}$ , 0.2 cm, in Methanol

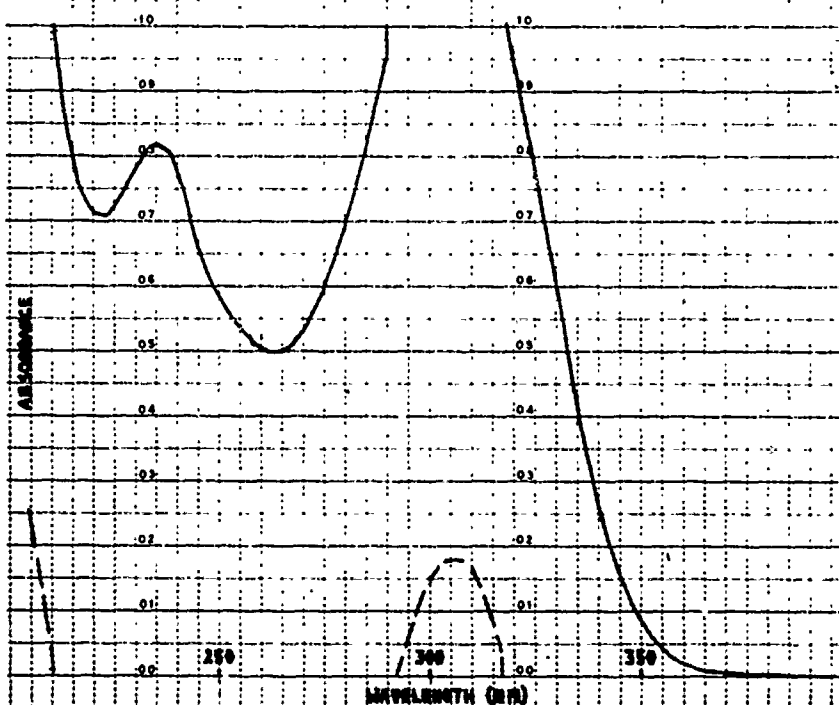


Figure A-15.  $\beta$ -(Bromomethyl)benzylidenemalononitrile, 266  $\mu\text{g/ml}$ , 0.1 cm, in Methanol

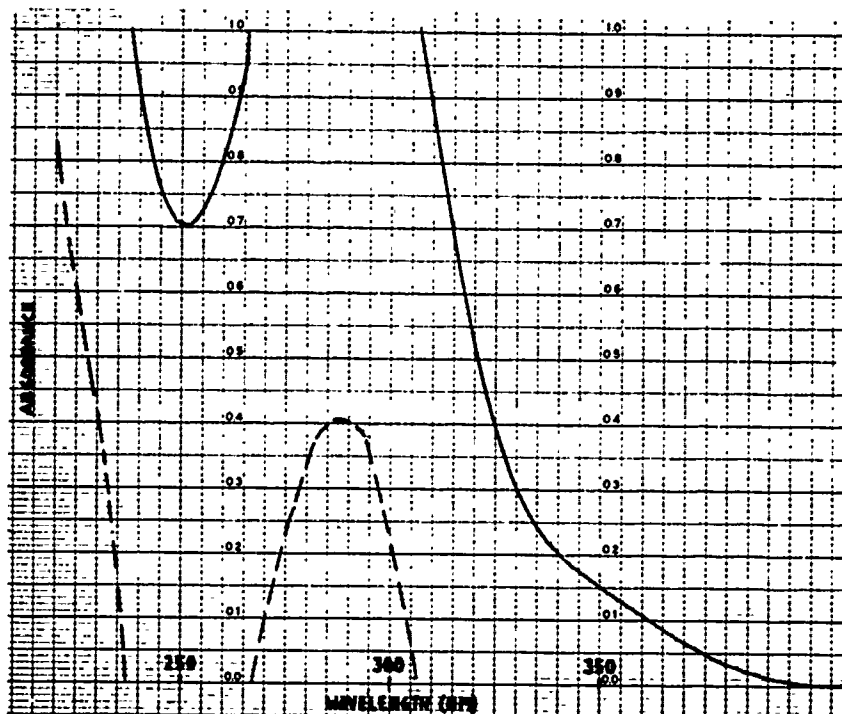


Figure A-16.  $\beta$ -(Bromomethyl)benzylidenemalononitrile + DEAEM,  
266  $\mu\text{g/ml}$ , 0.1 cm, in Methanol

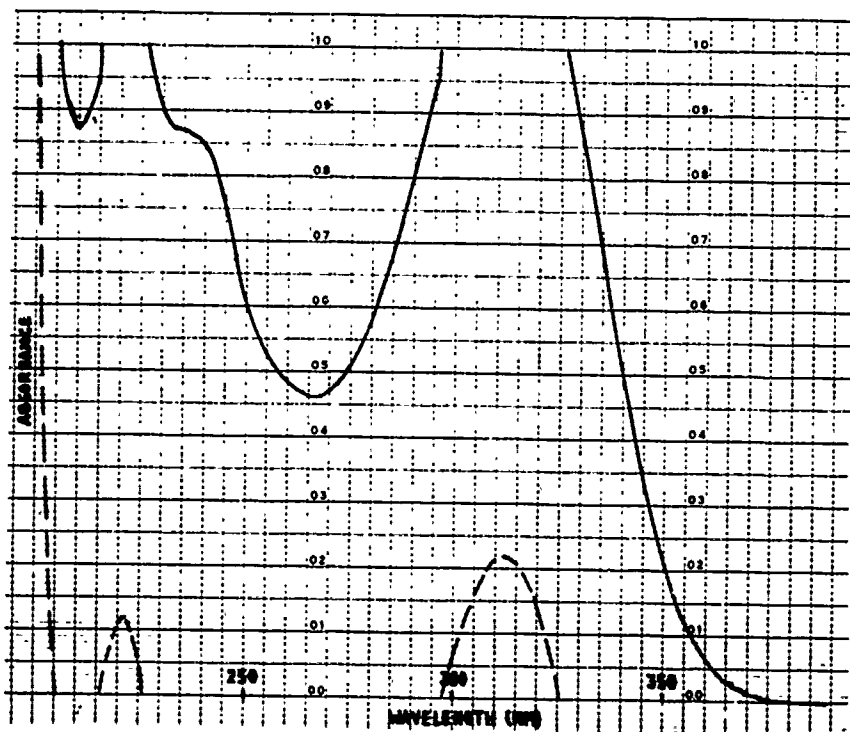


Figure A-17.  $\beta$ -(Bromomethyl)-4-Chlorobenzylidenemalononitrile,  
282  $\mu\text{g/ml}$ , 0.1 cm, in Methanol

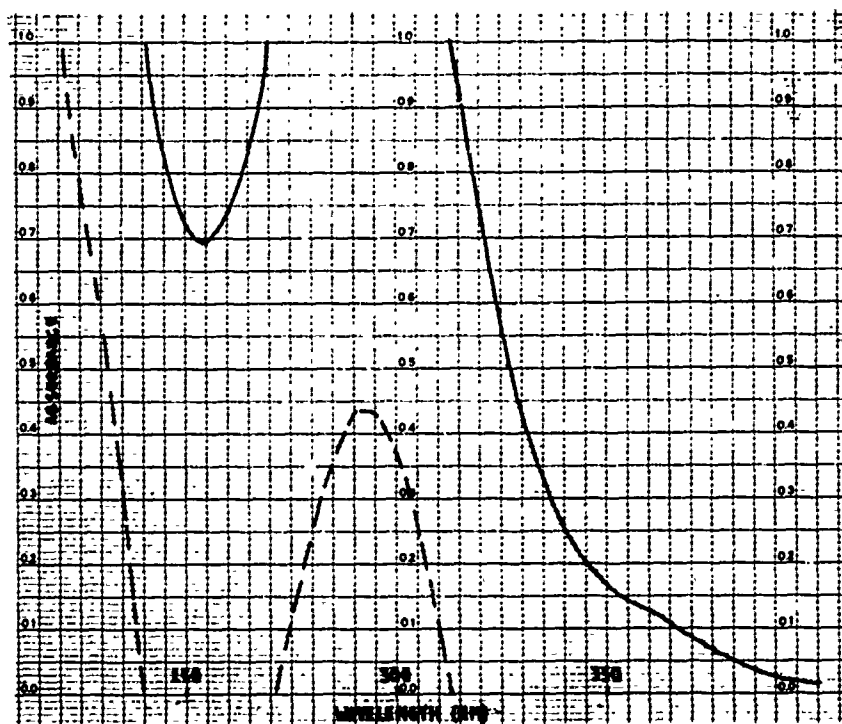


Figure A-18.  $\beta$ -(Bromomethyl)-4-Chlorobenzylidenemalononitrile + DEAEM,  
282  $\mu\text{g/ml}$ , 0.1 cm, in Methanol

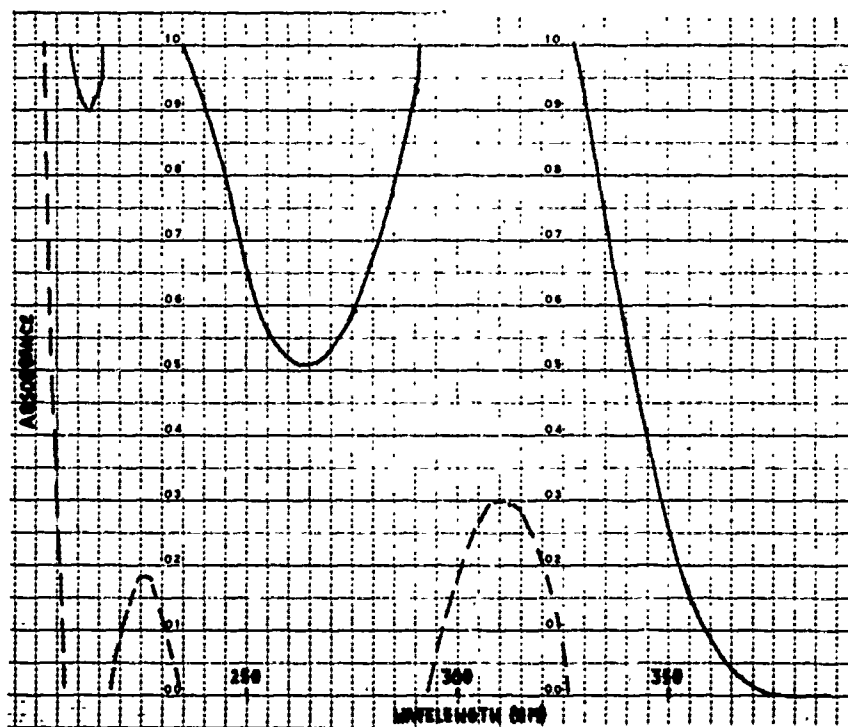


Figure A-19.  $\beta$ -(Bromomethyl)-4-Bromobenzylidenemalononitrile,  
328  $\mu\text{g/ml}$ , 0.1 cm, in Methanol



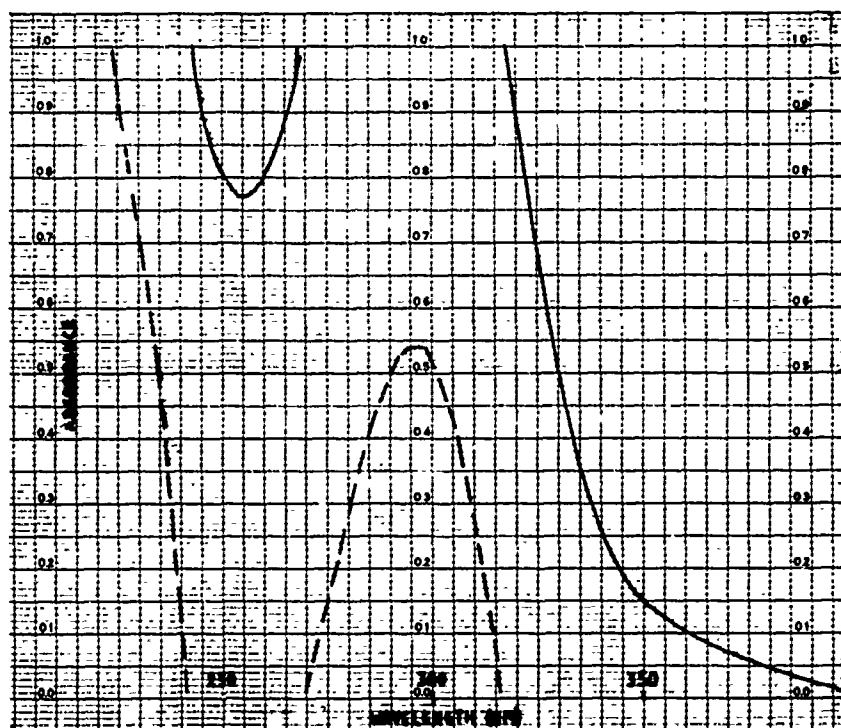


Figure A-20.  $\beta$ -(Bromomethyl)-4-Bromobenzylidenemalononitrile + DEAEM, 328  $\mu\text{g/ml}$ , 0.1 cm, in Methanol

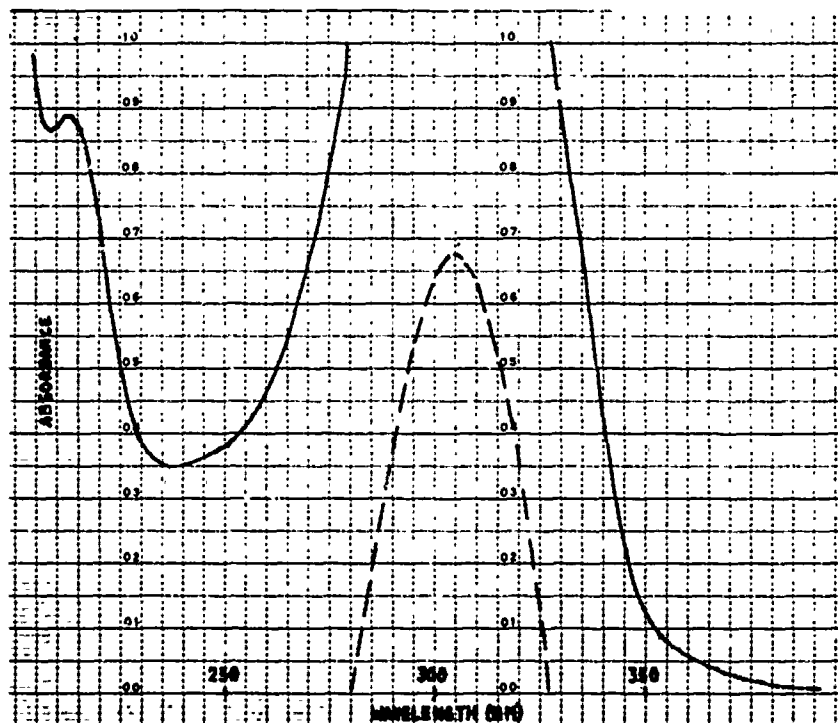


Figure A-21. 4-Nitrobenzylidenemalononitrile, 84.4  $\mu\text{g/ml}$ , 0.2 cm, in Methanol

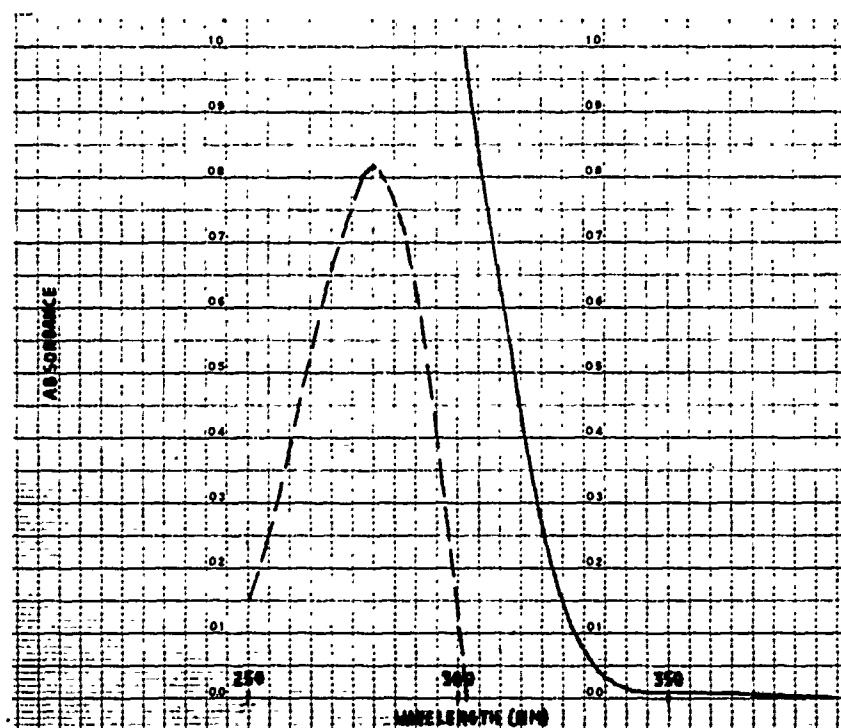


Figure A-22. 4-Nitrobenzylidenemalononitrile + DEAEM,  
84.4  $\mu\text{g/ml}$ , 0.2 cm, in Methanol

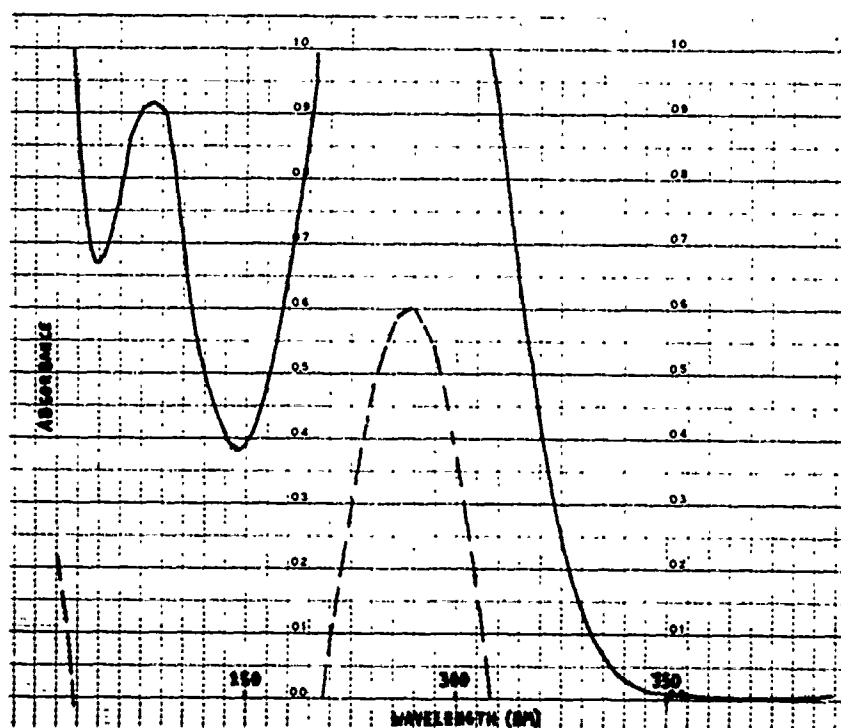


Figure A-23.  $\beta$ -Methylbenzylidenemalononitrile, 101.5  $\mu\text{g/ml}$ ,  
0.2 cm, in Methanol

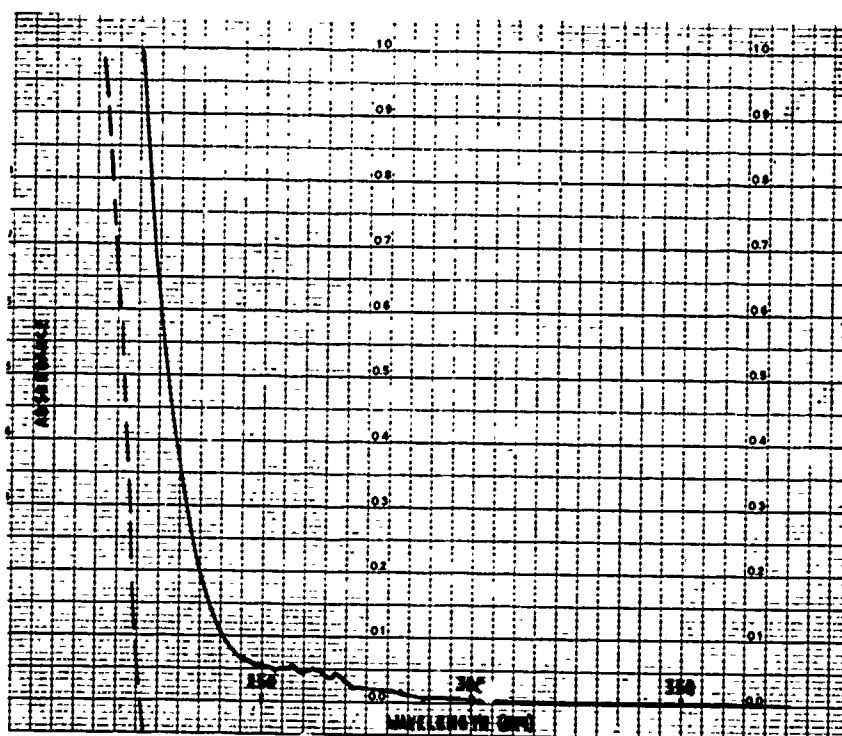


Figure A-24.  $\beta$ -Methylbenzylidenemalononitrile + NaCN,  
90.8  $\mu\text{g/ml}$ , 0.2 cm, in Methanol

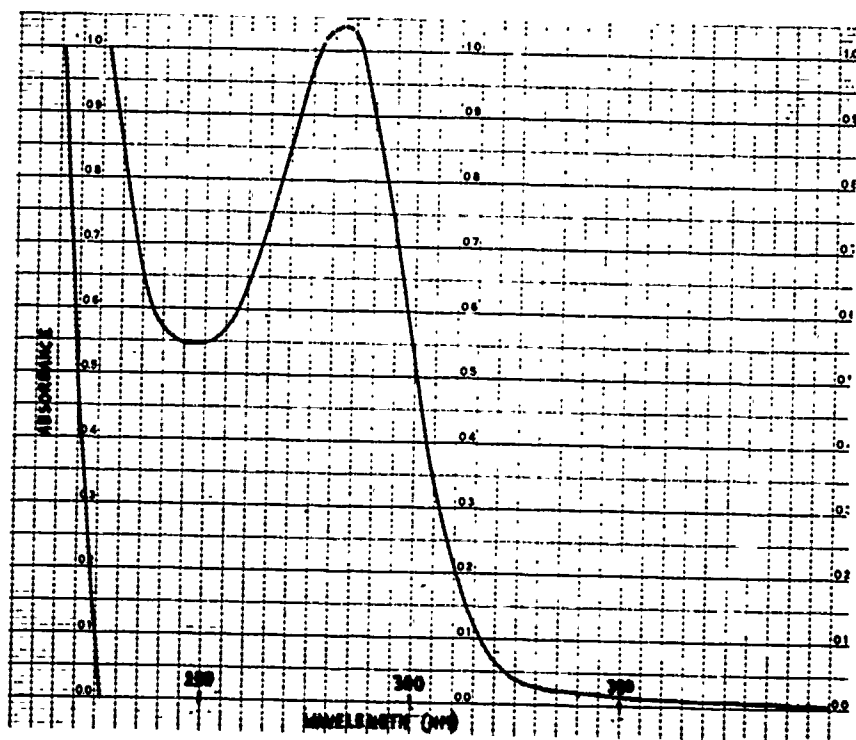


Figure A-25.  $\beta$ -Methylbenzylidenemalononitrile + NaCN + DEAEM,  
90.8  $\mu\text{g/ml}$ , 0.2 cm, in Methanol-1% Acetic acid

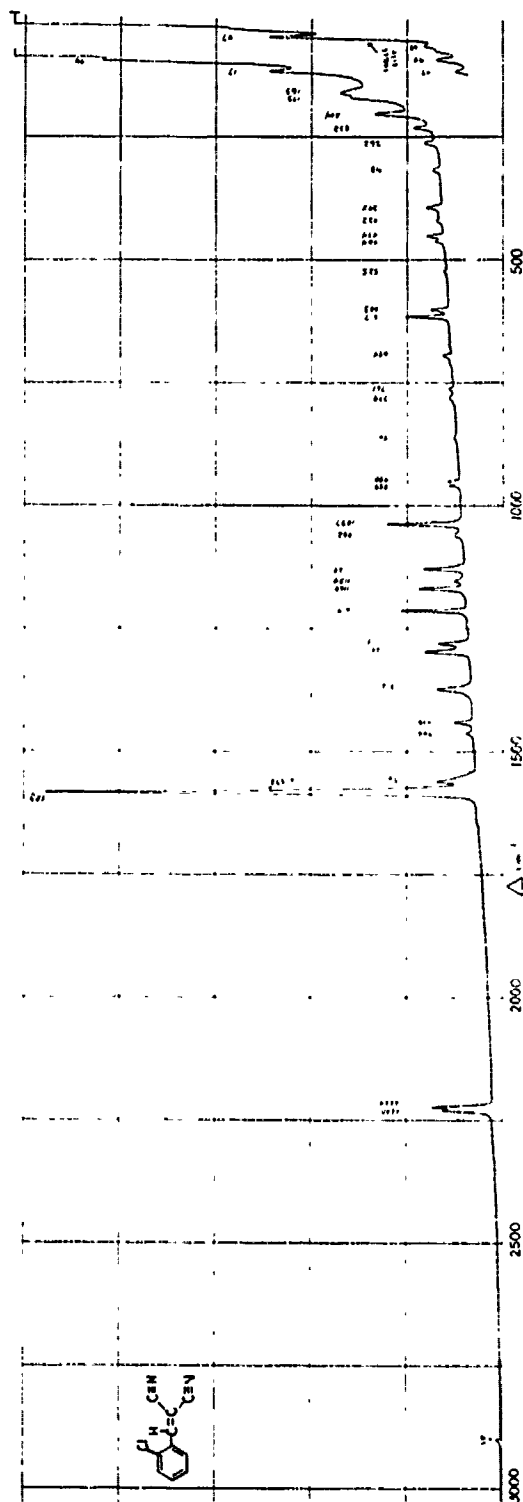
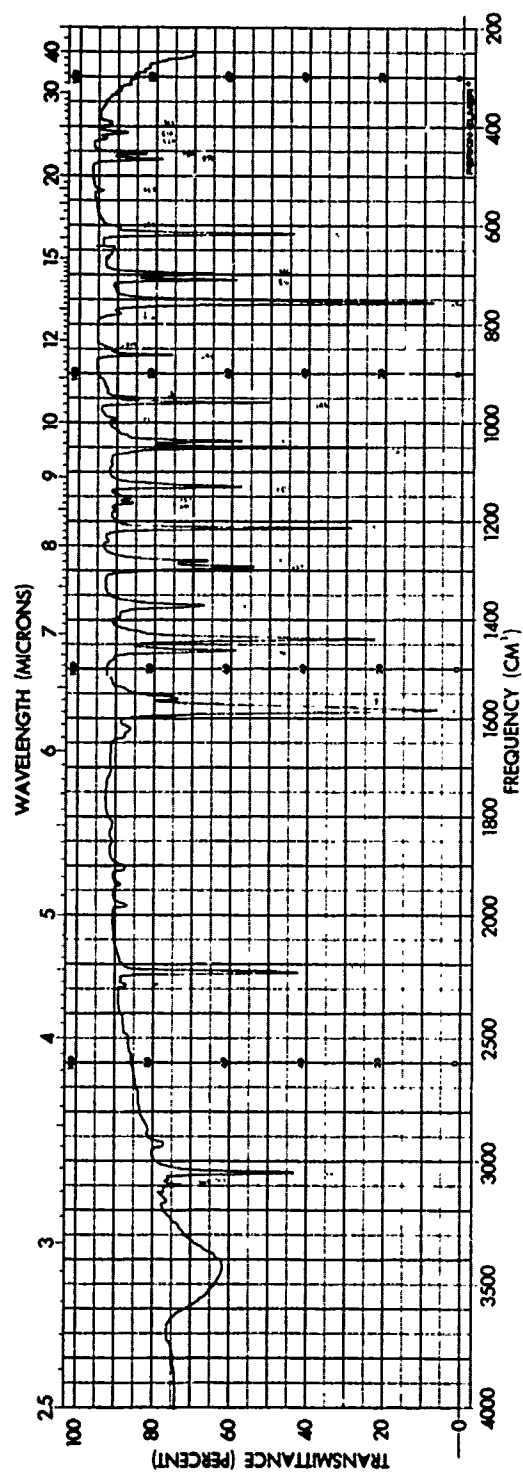


Figure A-26. *o*-Chlorobenzylidenemalononitrile (CS)

- Infrared spectrum in KBr.
- Raman spectrum, solid-sens.  $1.7 \times 10$ , S.W.  $5 \text{ cm}^{-1}$ , pen  $0.5 \text{ sec}$ , scan  $1 \text{ cm}^{-1}/\text{sec}$ .

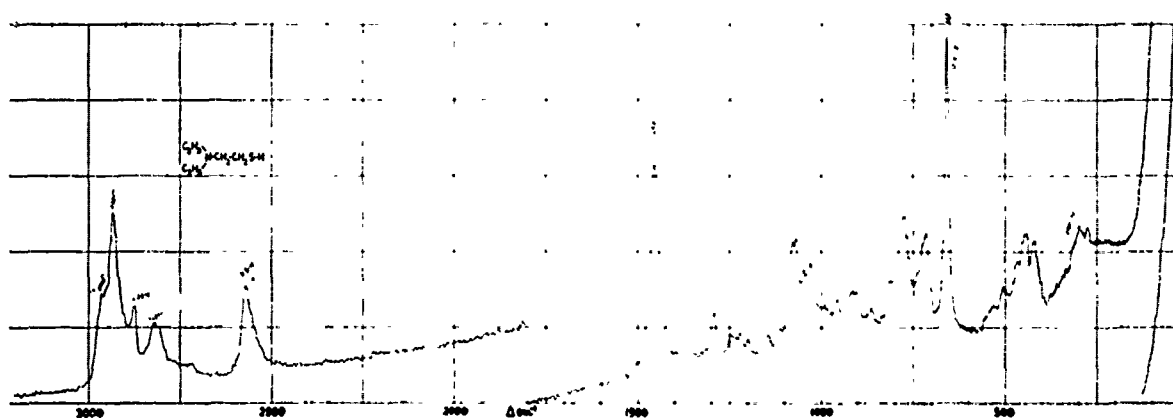
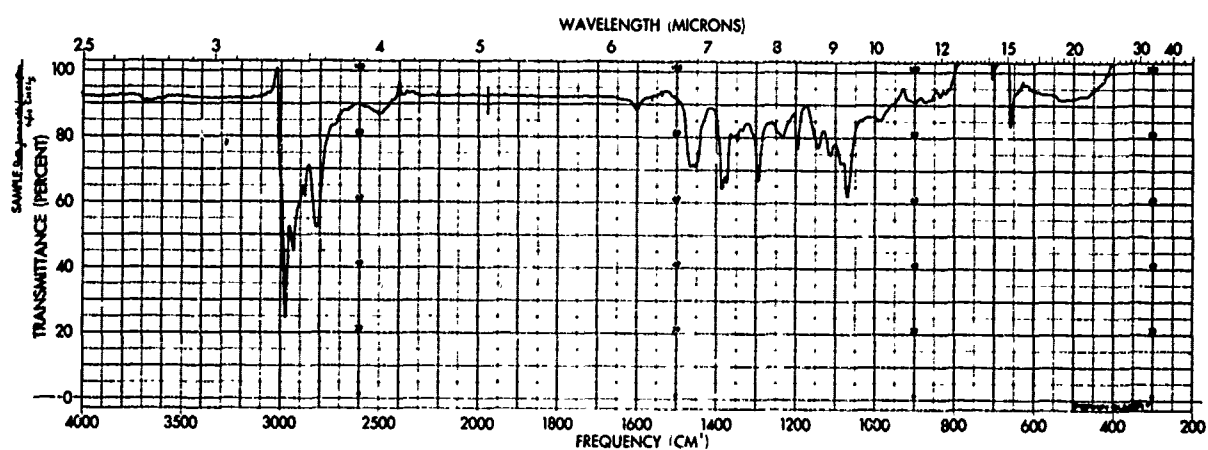
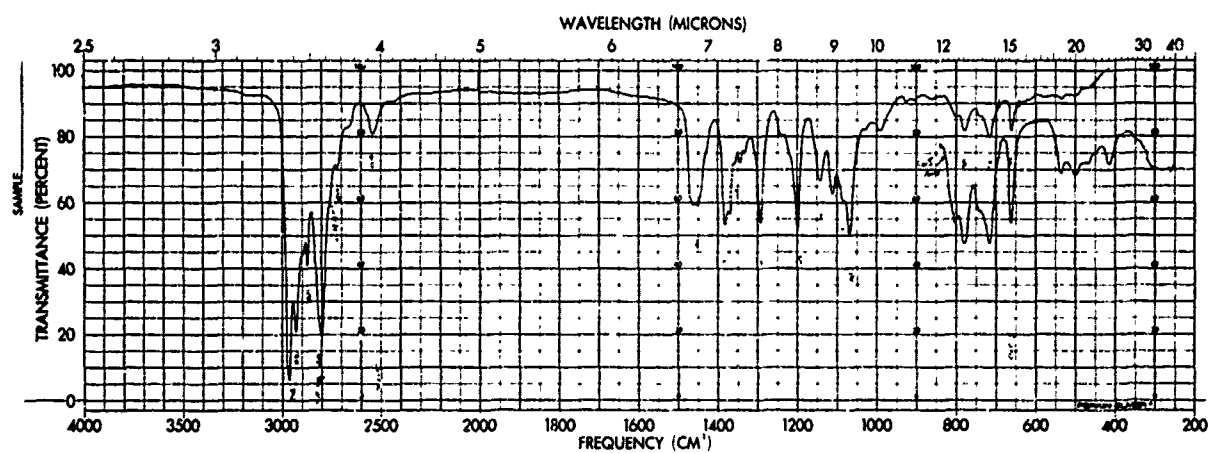


Figure A-27. 2-Diethylaminoethyl Mercaptan (DEAEM)

- a. Infrared spectrum—liquid, capillary film.
- b. Infrared spectrum in chloroform, 0.265 M, 0.104-mm cell.
- c. Raman spectrum, liquid—sens.  $1.4 \times 200$ , S.W.  $5 \text{ cm}^{-1}$ , pen  $5 \text{ sec}$ , scan  $1 \text{ cm}^{-1}/\text{sec}$ .

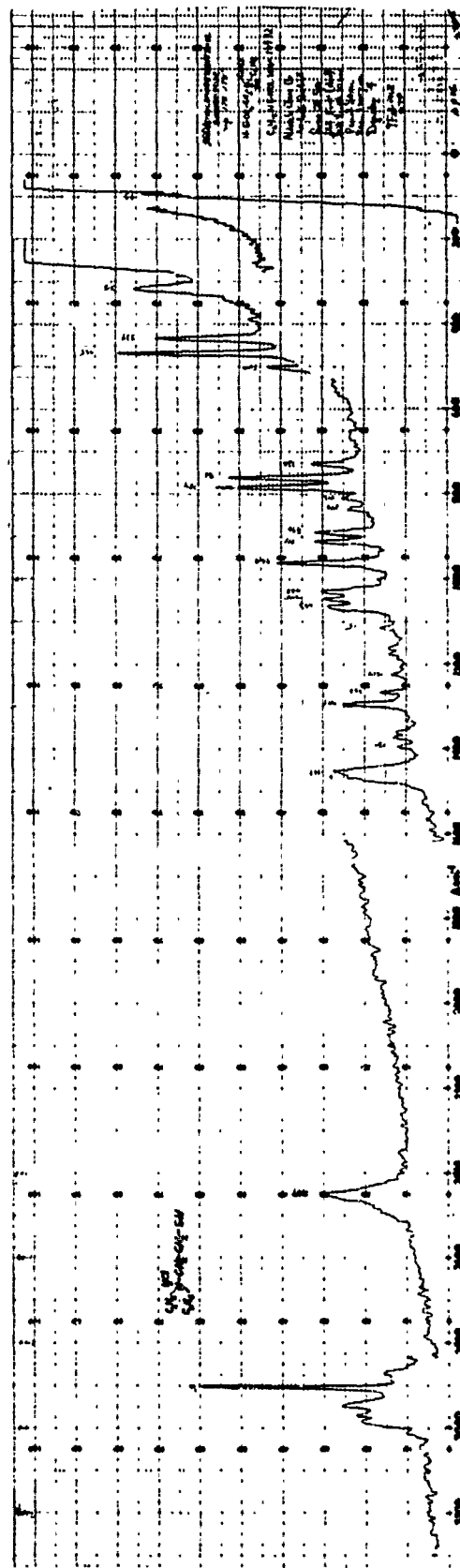
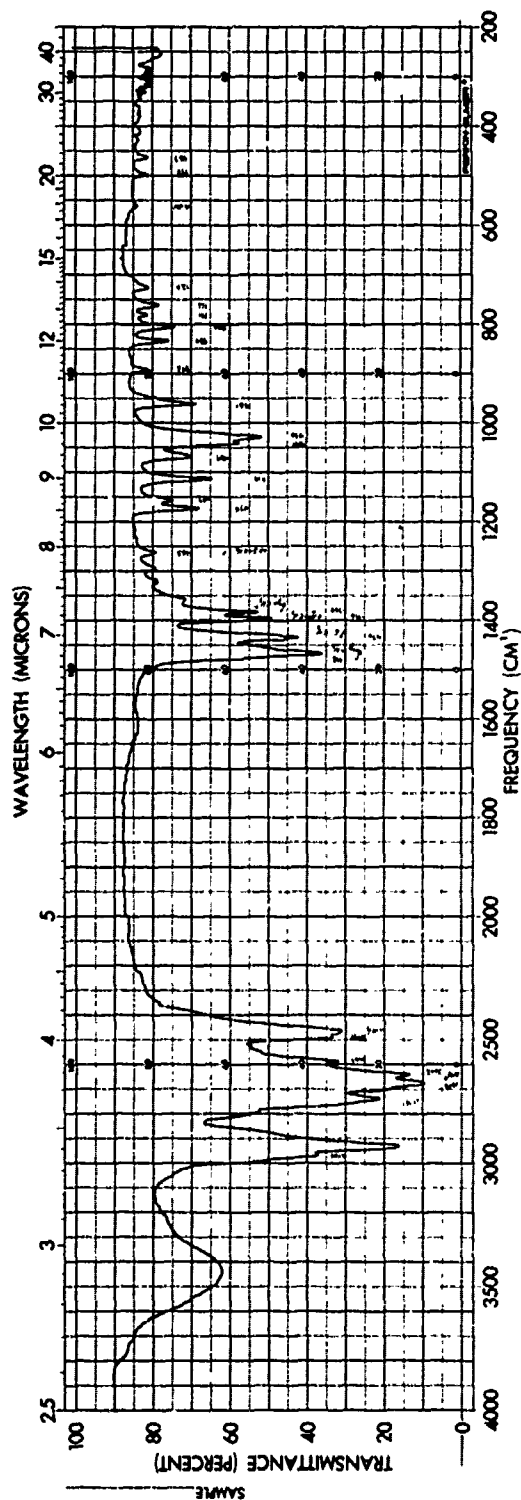


Figure A-28. 2-Diethylaminoethyl Mercaptan Hydrochloride

- Infrared spectrum in KBr.
- Raman spectrum, solid-sens.  $2 \times 500$ , S.W.  $5 \text{ cm}^{-1}$ , pen  $20 \text{ sec}$ , scan  $1 \text{ cm}^{-1}/\text{sec}$ .

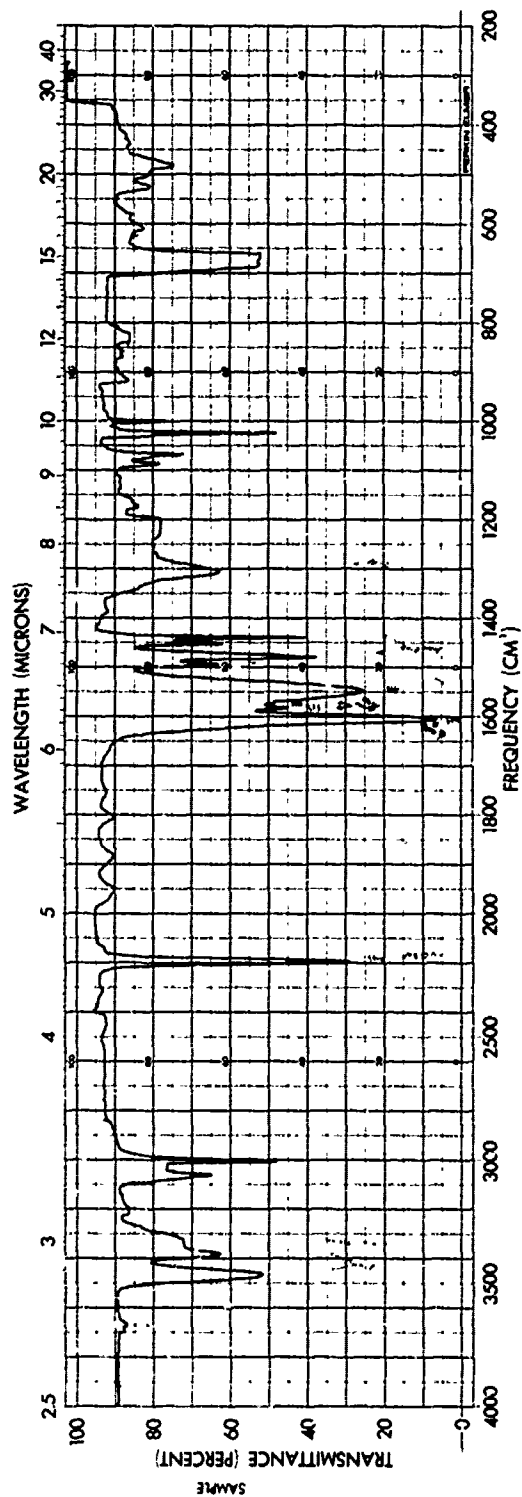
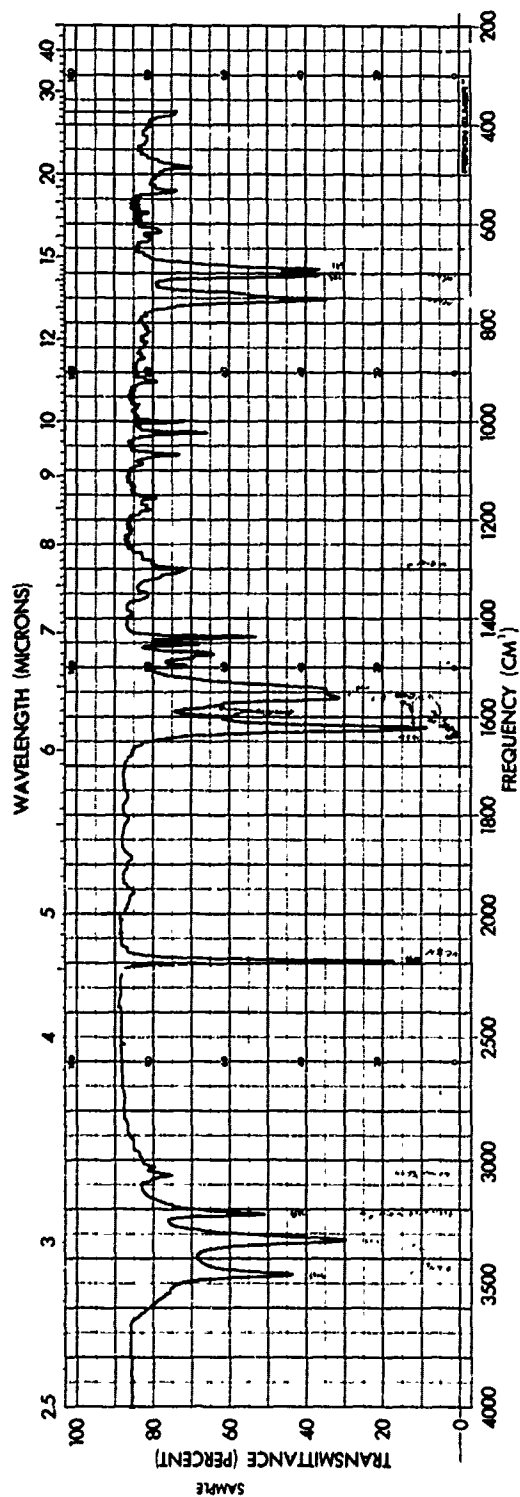


Figure A-29. Compound (IV)

- a. Infrared spectrum in KBr.
- b. Infrared spectrum in chloroform, 0.192-mm cell.

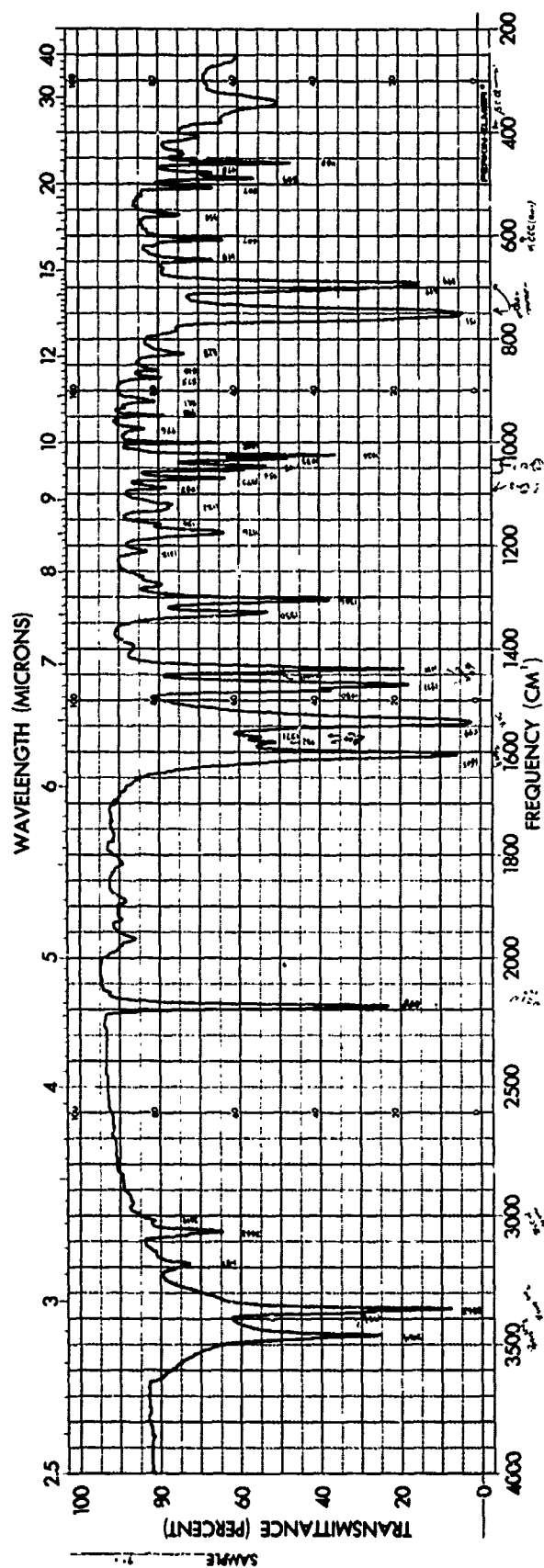


Figure A-30. Compound (V)—Infrared Spectrum in KBr



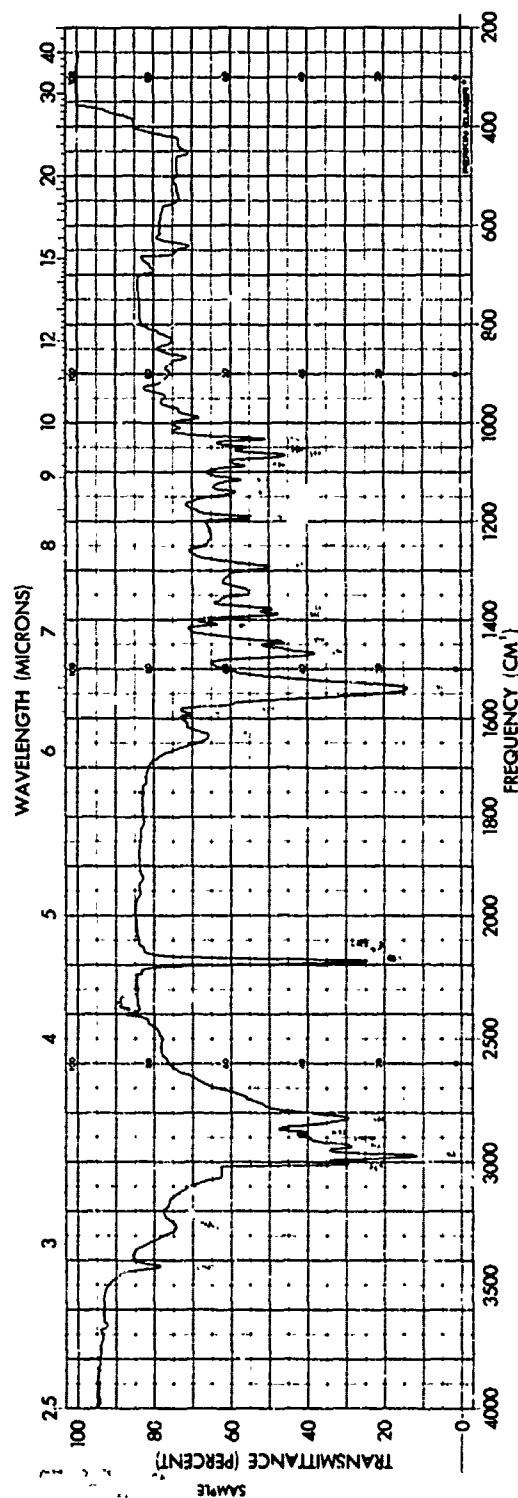
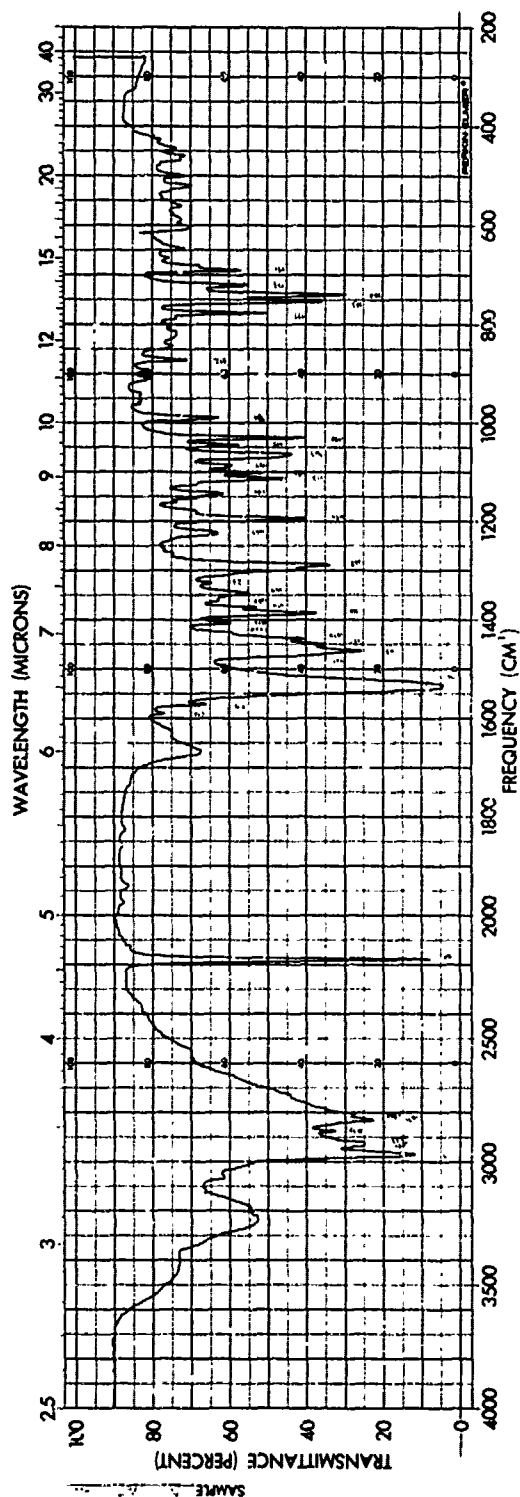


Figure A-31. Compound (I)-CS(DEAEM)<sub>2</sub>

a. Infrared spectrum in KBr.

b. Infrared spectrum in chloroform, 0.126 M, 0.154-mm cell.

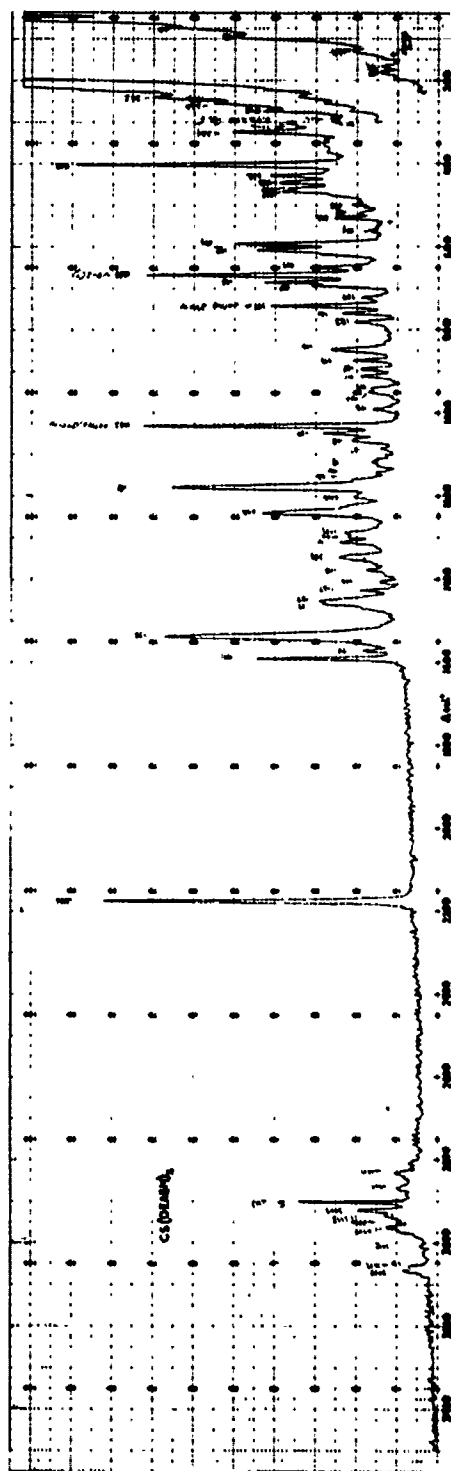
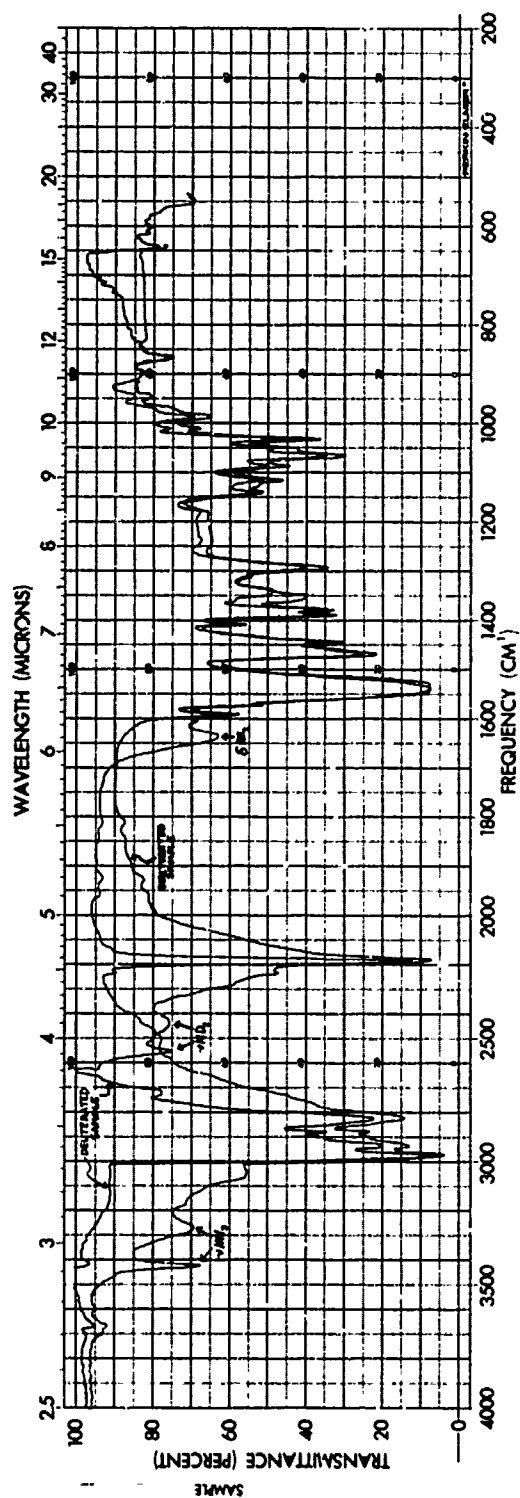


Figure A-31. Continued

- c. Infrared spectrum of a deuterated sample in chloroform, 0.063 M, 0.505-mm cell.
- d. Raman spectrum, solid-sens. 2.4 x 200, S.W. 5 cm<sup>-1</sup>, pen 15 sec, scan 0.5 cm<sup>-1</sup>/sec.

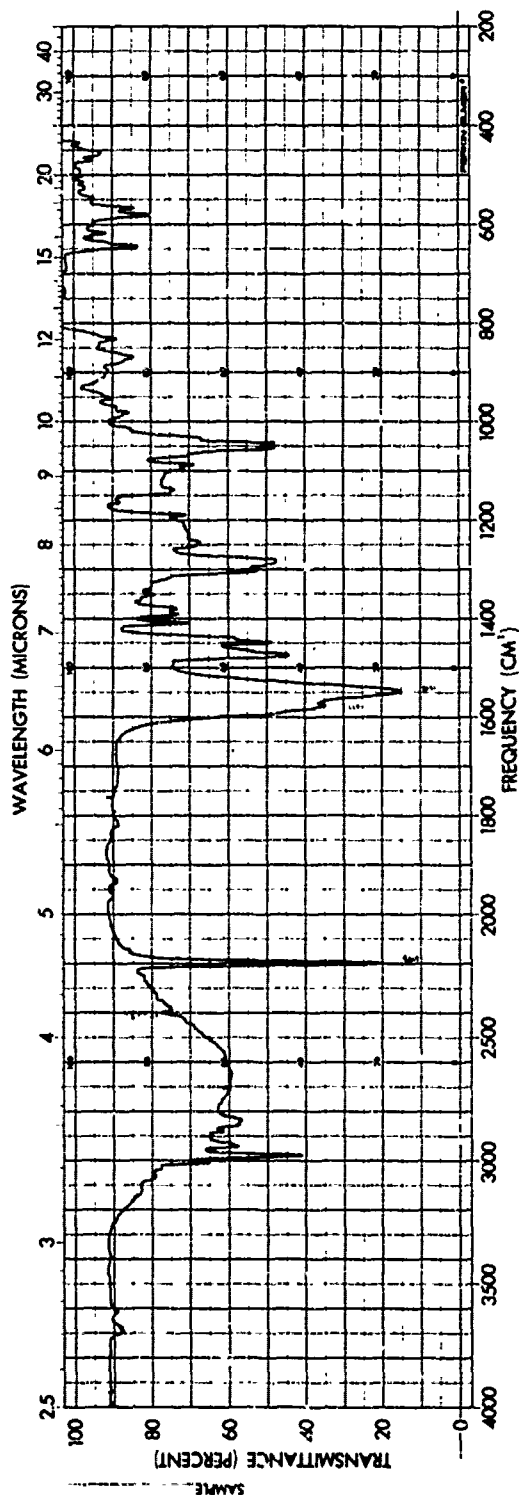
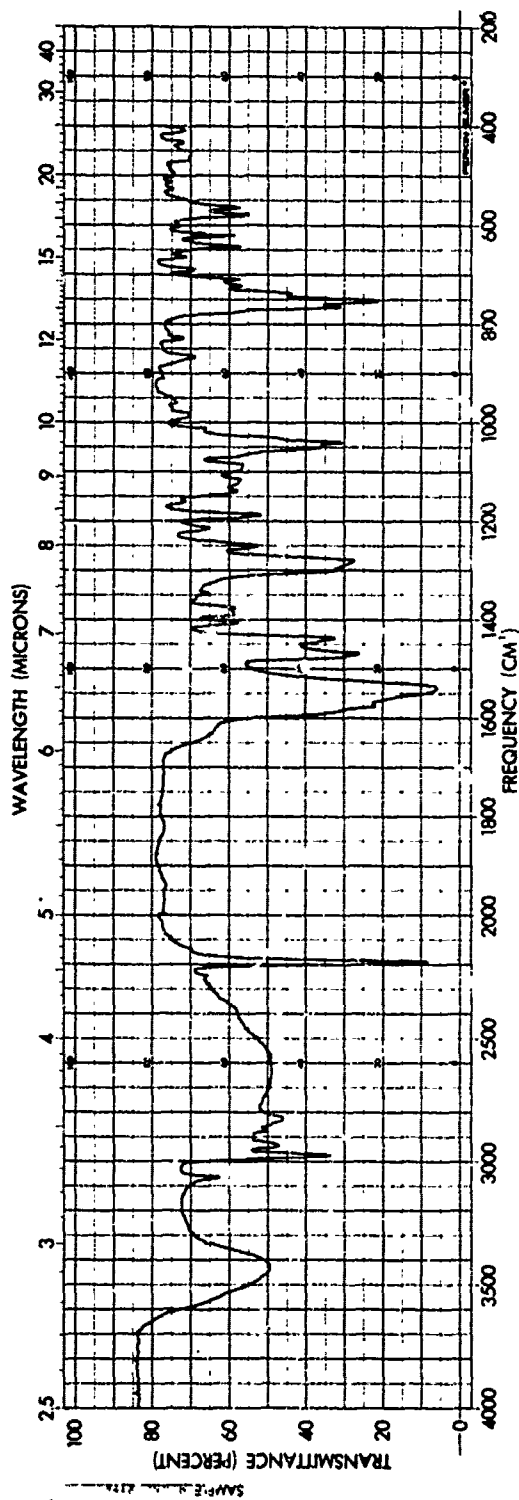


Figure A-32. Compound (VI)-(CS)<sub>2</sub>DEAEM

- a. Infrared spectrum in KBr.
- b. Infrared spectrum in chloroform, 0.192-mm cell.

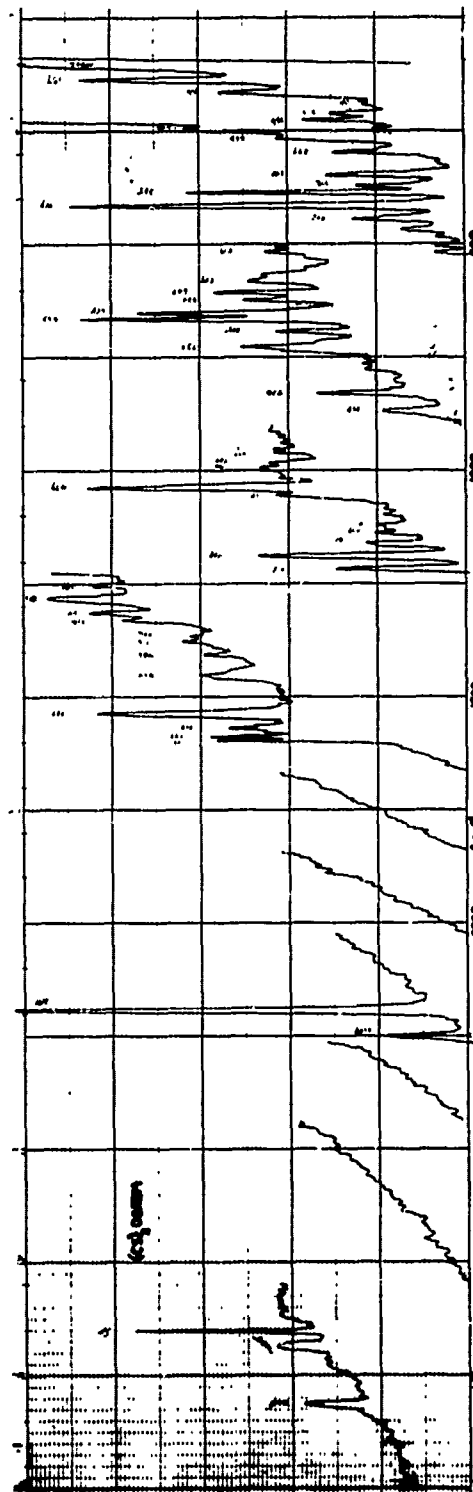
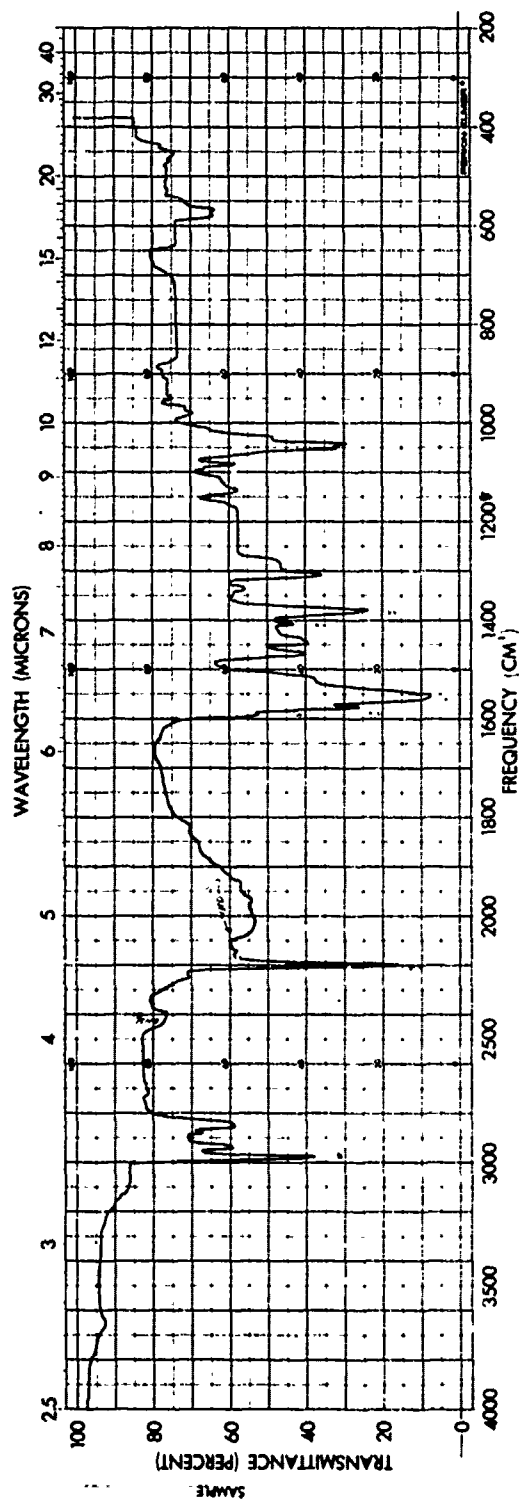


Figure A-32. Continued

- c. Infrared spectrum of a deuterated sample in chloroform, 1.0-mm cell. (The spectrum of an undeuterated sample is also shown.)
- d. Raman spectrum, solid-sens.  $2 \times 500$ , S.W.  $5 \text{ cm}^{-1}$ , pen 15 sec, scan  $0.5 \text{ cm}^{-1}/\text{sec}$ .

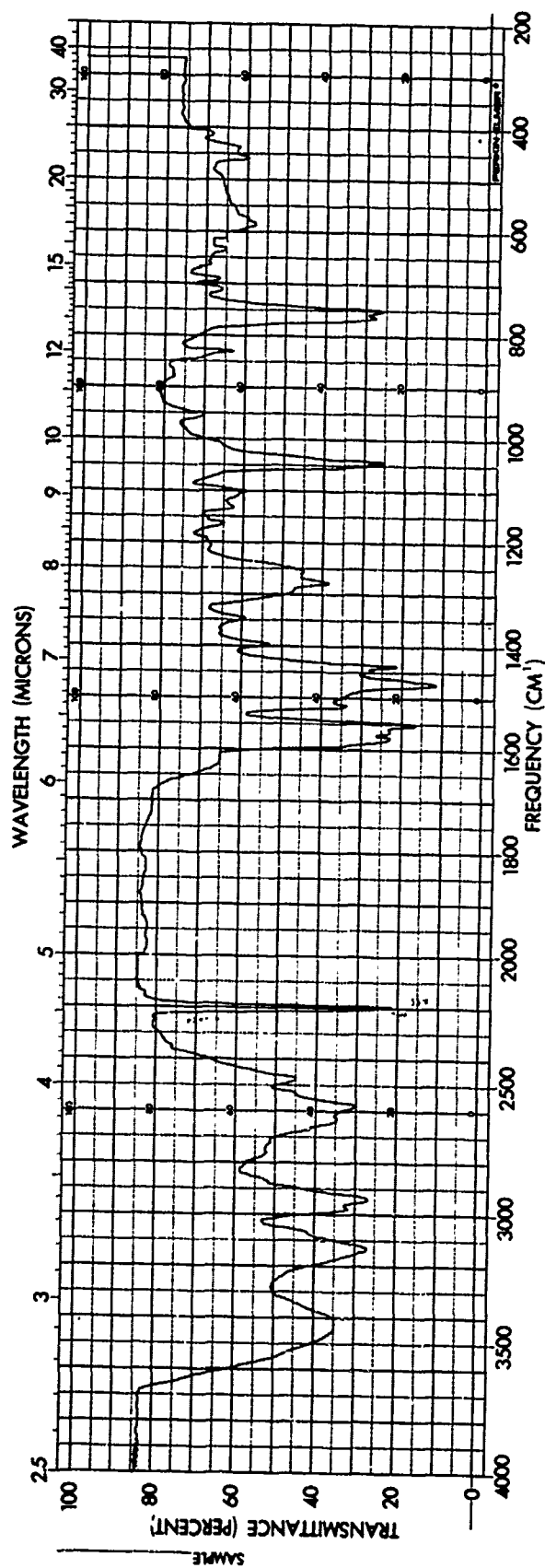


Figure A-33. Compound (VII)-(CS)<sub>2</sub> DEAEM·HCl Infrared Spectrum in KBr